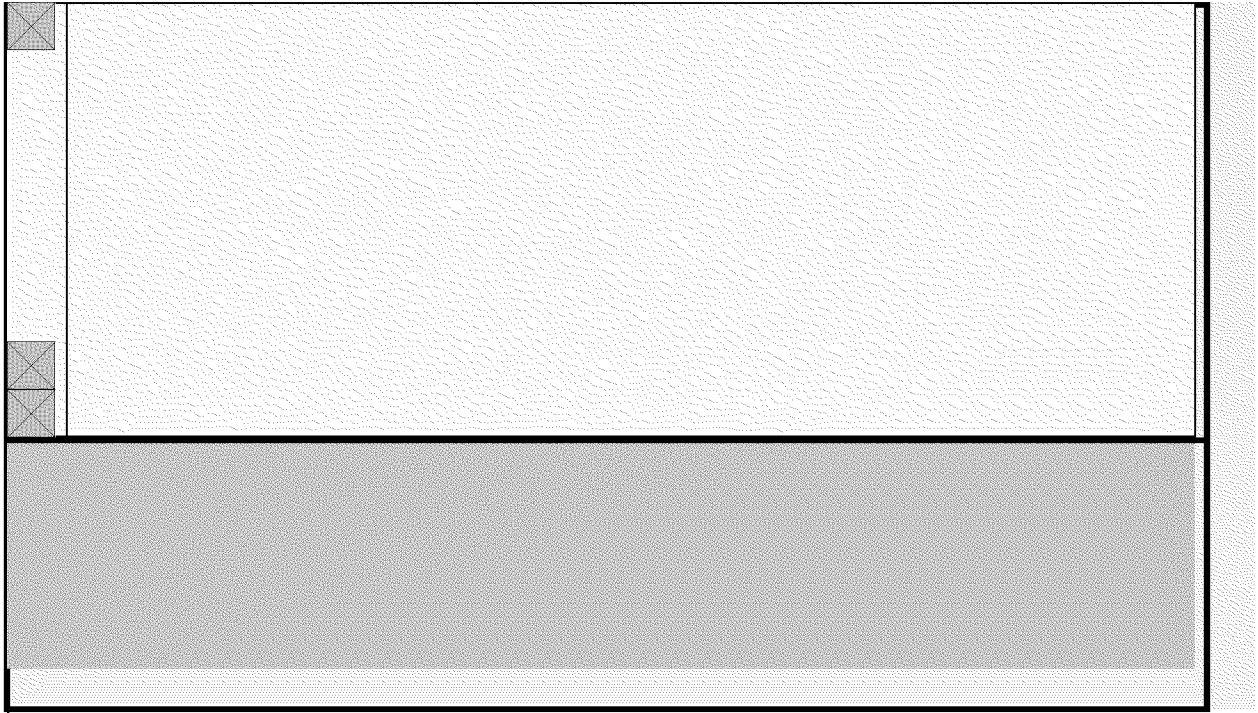**To:** Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Jay Ritchie - GoMRI
Sent: Tue 6/16/2015 11:45:02 AM
Subject: Santa Barbara Spill, Microbes, and Seafood -- GoMRI eNews: June 16, 2015

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Holder, Edith[holder.edith@epa.gov]
From: Musson, Steve
Sent: Mon 6/15/2015 12:22:53 PM
Subject: FW: HASP Annual Review Due

Robyn,

I haven't gotten this HASP to sign yet. Do you have it?

Steve

From: Holder, Edith
Sent: Monday, June 01, 2015 3:14 PM
To: Musson, Steve
Subject: RE: HASP Annual Review Due

Steve,

I have signed it electronically and sent it on to Robyn. I assume that you will send it back to me after you sign. Then I will print it for the box outside the laboratory. Correct?

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Musson, Steve
Sent: Friday, May 29, 2015 10:44 AM
To: Holder, Edith
Cc: Conmy, Robyn; Venkatapathy, Raghuraman; Schubauer-Berigan, Joseph; Meghan Welch
Subject: RE: HASP Annual Review Due

Hi Edie,

Thanks for providing all of the information. We (SHEM) will keep hunting down official SDS's for these. However, we don't need to hold up the HASP revision for that.

This HASP is ready for the approval process. I've attached it as both a word version and a pdf version. The pdf version allows the approvers to sign electronically if you wish to route it around via email for electronic signatures. Either way, hand or electronic signatures, I would be the last person to sign so I can make a copy of the cover page for our records.

If you need anything or have any questions, please give me a call. X7969

Steve

Stephen Musson, PhD, CIH, CHMM

Safety, Health, and Environmental Management Program Manager

US EPA National Risk Management Research Laboratory

26 W. Martin Luther King Drive

Cincinnati OH 45268

513-569-7969

From: Holder, Edith
Sent: Thursday, May 21, 2015 2:36 PM
To: Musson, Steve
Cc: Conmy, Robyn; Venkatapathy, Raghuraman; Schubauer-Berigan, Joseph; Meghan Welch
Subject: RE: HASP Annual Review Due

I found these on the EPA List of NCP Products

http://www2.epa.gov/emergency-response/alphabetical-list-ncp-product-schedule-products-available-use-during-oil-spill

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Musson, Steve
Sent: Wednesday, May 20, 2015 4:25 PM
To: Holder, Edith
Cc: Conmy, Robyn; Venkatapathy, Raghuraman; Schubauer-Berigan, Joseph; Meghan Welch
Subject: RE: HASP Annual Review Due

Thanks Edie,

I will keep looking too, maybe I can find them online somewhere.

Steve

From: Holder, Edith
Sent: Tuesday, May 19, 2015 4:02 PM
To: Musson, Steve
Cc: Conmy, Robyn; Venkatapathy, Raghuraman; Schubauer-Berigan, Joseph; Meghan Welch
Subject: RE: HASP Annual Review Due

Here are the records in our lab.

Biodispers and Dispersit SPC 1000 are old dispersants in our lab and are lines 11 and 12 of last year's HASP. The MSDS are not in my current notebook as we are not currently using them, but we will look for them in boxes of old records.

FFT Solution was just received in our lab, and we will follow up with the manufacturer for the SDS.

The SDS has been requested from the manufacturer of EPA Oil Field Solution, but we have not received it. An additional contact will be made.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Musson, Steve
Sent: Tuesday, May 19, 2015 10:41 AM
To: Holder, Edith
Cc: Conmy, Robyn; Venkatapathy, Raghuraman; Schubauer-Berigan, Joseph
Subject: RE: HASP Annual Review Due

Hi Edie,

There were many new dispersants. I appreciate you taking the time to add them to the HASP. I want to stress that the lab is not allowed to receive any new chemicals until the HASP is revised before they are received. Otherwise EPA and Pegasus are not meeting OSHA regulations for

Hazcom.

I tried to find as many MSDS/SDS online that I could for the dispersants/SWAs. But I have highlighted several that we do not have a MSDS/SDS on file and I could not find online. Please provide a copy of those. Once we get those we will be able to route the HASP. Until then, no work is allowed using these highlighted items.

Steve

From: Holder, Edith
Sent: Thursday, May 14, 2015 2:36 PM
To: Musson, Steve
Cc: Conmy, Robyn
Subject: RE: HASP Annual Review Due

Steve,

Enclosed is a revised HASP. During the last year we have received more oils, dispersants, and SWA. Those products have been added in tables by category at the end of the chemical list. There are no other changes.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Musson, Steve
Sent: Wednesday, May 13, 2015 10:09 AM
To: DelaCruz, Armah; Nadagouda, Mallikarjuna; Schaefer, Frank; Silvestri, Erin; Pressman, Jonathan; Wahman, David; Feldhake, David; quintero.maria@azdeq.gov; Shanks, Orin; Kelty, Catherine; Shoemaker, Jody; Varma, Rajender; Donohue, Maura; Pfaller, Stacy; Jewett, David; Hargrove, Kristie; Al-Abed, Souhail; Pinto, Patricio; Brooks, Michael; Wood, Lynn; Conmy, Robyn; Holder, Edith; Zaffiro, Alan; Batt, Angela; See, Mary Jean
Subject: HASP Annual Review Due

Everyone,

You are getting this email because your HASP is due for its annual review in May or June.

One of the staff listed below for each HASP, please take a moment to review the HASP and respond to this email by either:

1. State "The HASP is current and no changes need to be made"

2. State "The HASP is no longer necessary, please inactivate it"

3. Send the HASP back to me with any changes that need to be made to revise it.

Thanks,

Steve

Stephen Musson, PhD, CIH, CHMM

Safety, Health, and Environmental Management Program Manager

US EPA National Risk Management Research Laboratory

26 W. Martin Luther King Drive

Cincinnati OH 45268

513-569-7969

Division	TSA #	SR #	Rev #	Title	Date Review Due	Principal Investigator #1	Principal Investigator #2	Principal Investigator #3	Preparer	Branch	Expir Date
MCE	2013 087	R	1	Cyanobacteria and their Cyanotoxins	6/16/2014	de la Cruz, Armah A.			de la Cruz, Armah A.	MiE	3/31
WSW	2013 030	R	4	Sulfate and Phosphate Removal using novel synthesized media	6/17/2014	Mohan, Gayathri Ram	Nadagouda,Mallikarjuna		Mohan, Gayathri Ram	IO	3/31/
TCA	2013 033		2	Optimization of Bacillus anthracis Spore Recovery from Soil	6/18/2014	Schaefer, Frank	Silvestri, Erin		Feldhake, David	None Chosen	4/30/
WSW	2013 045	R	2	Chloraminated Drinking Water Distribution System Nitrification	5/15/2014	Pressman,Jonathan	Wahman,David		Quinter, Kalya	TTE	6/30/
WSW	2013 047	R	0	Genome Fragment Enrichment	6/30/2014	Shanks,Orin			Kelty, Catherine	MCB	6/30/
MCE	2013 062	R	0	Measuring Sucralose In Recreational Waters To Identify Human-Based Fecal Pollution: A Pilot Study	6/15/2014	Shoemaker,Jody			Shoemaker,Jody	CLRB	3/31/
STD	2014 003		0	Highly Selective Photosynthesis Processes over Visible-Light-Induced Micro- and Nano-structured Photocatalysts	5/29/2014	Baig,Nasir	Varma,Rajender		Baig,Nasir	GPB	1/31/

MCEARD 2014 014	General Laboratory Practices Associated with Proteomic Research	5/30/20..	Donohue, Maura, Stacy		Donohue	NRMRL	1/...
GWERD 2014 023	Laboratory 4	5/30/20..	Jewett, David		Hargrove	ARTSB	30/...
LRPCD 2014 024	Metal Migration from Drinking Water Treatment Plant (DWTP) Sludges and Landfill Soils under Different Redox Conditions	6/4/2014	Al-Abed, Souhail		Pinto, Pat	WMD	30/...
GWERD 2014 032	Predicting DNAPL Source Zone and Plume Response Using Site Measured Characteristics	6/30/20..	Brooks, Michael, Lynn		Wood, Lynn	SRB	6/30/...
LRPCD 2014 033	Oil Spill Research Including Work with Dispersants, Surface Washing Agents (SWAs), and Oil Degrading Microbes	6/30/20..	Conmy, Robyn		Holder, E	LSMB	6/30/...
SRMD 2014 039	Second Laboratory Demonstration for Microcystins in Drinking Water using Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry	6/30/20..	Adams, William		Zaffiro, A	TSC	6/30/...
EERD 2014 016	Aquatic Studies Analytical Support using Solid Phase Extraction and Gas Chromatography/Mass Spectrometry	6/30/20..	Batt, Angela		See, Mary Jean	MIRB	6/30/...

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Barth, Edwin[Barth.Ed@epa.gov]; Kremer, Fran[Kremer.Fran@epa.gov]
From: Fitzpatrick, Faith
Sent: Fri 6/12/2015 8:15:32 PM
Subject: Re: Colleague review of USGS report "Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments--Review of the Science and Future Research Needs"
OPA OFR 2015_1076.pdf

Hello, here is the final report. It should be uploaded to USGS pubs warehouse in a few weeks. Regards, Faith

On Wed, Oct 22, 2014 at 7:04 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hi Faith,

Attached are my edits and comments to the OPR report. As per our last correspondence, I have sent it on to EPA OEM for policy review but have not received feedback as of yet. Their input will be valuable as the report touches on the use of adding natural inorganic particles as a potential countermeasure and means of natural dispersion. Given that fate of OPA could result in sinking and the US currently does not approve sinking agents, I thought OEM could provide some perspective for all of us.

Also, did we decide on a new time for a call or is EPA to review your ppt slides first? I am out of the office all next week.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

From: Faith [mailto:fafitzpa@usgs.gov]
Sent: Thursday, October 16, 2014 4:43 PM
To: Conmy, Robyn
Subject: RE: Colleague review of USGS report "Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments--Review of the Science and Future Research Needs"

Yes please do this. Appreciatively, Faith
(from smartphone)

On October 16, 2014 9:42:01 AM CDT, "Conmy, Robyn" <Conmy.Robyn@epa.gov> wrote:

Hi Faith,

In reviewing the document, I would like to request that EPA OSWER OEM also take a look at it to provide comments. Particularly Greg Wilson and Vanessa Principe who are well versed in OPA issues and have been participating on the calls with NAS (Doug Freedman (sp?)). Would this be permissible to you? If so, I will forward to them

Thanks,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Fitzpatrick, Faith [mailto:fafitzpa@usgs.gov]
Sent: Wednesday, September 24, 2014 9:27 AM
To: Conmy, Robyn
Cc: Barth, Edwin
Subject: Re: Colleague review of USGS report "Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments--Review of the Science and Future Research Needs"

Hi Robyn, I was saving Ed for the modeling reports which should be coming at the end of this week :), but I've cc'd Ed just in case! There isn't much modeling in this report--- there is a little bit but it is more a summary of the state of the science concerning oil-particle interactions -- other lab, flume, studies, etc. from freshwater to marine. Maybe there is someone else too. For this report it would be best to have someone that is familiar with past oil spills and sinking oil. Faith

Faith Fitzpatrick, Ph.D.

Research Hydrologist (Fluvial Geomorphology)

USGS WI Water Science Center
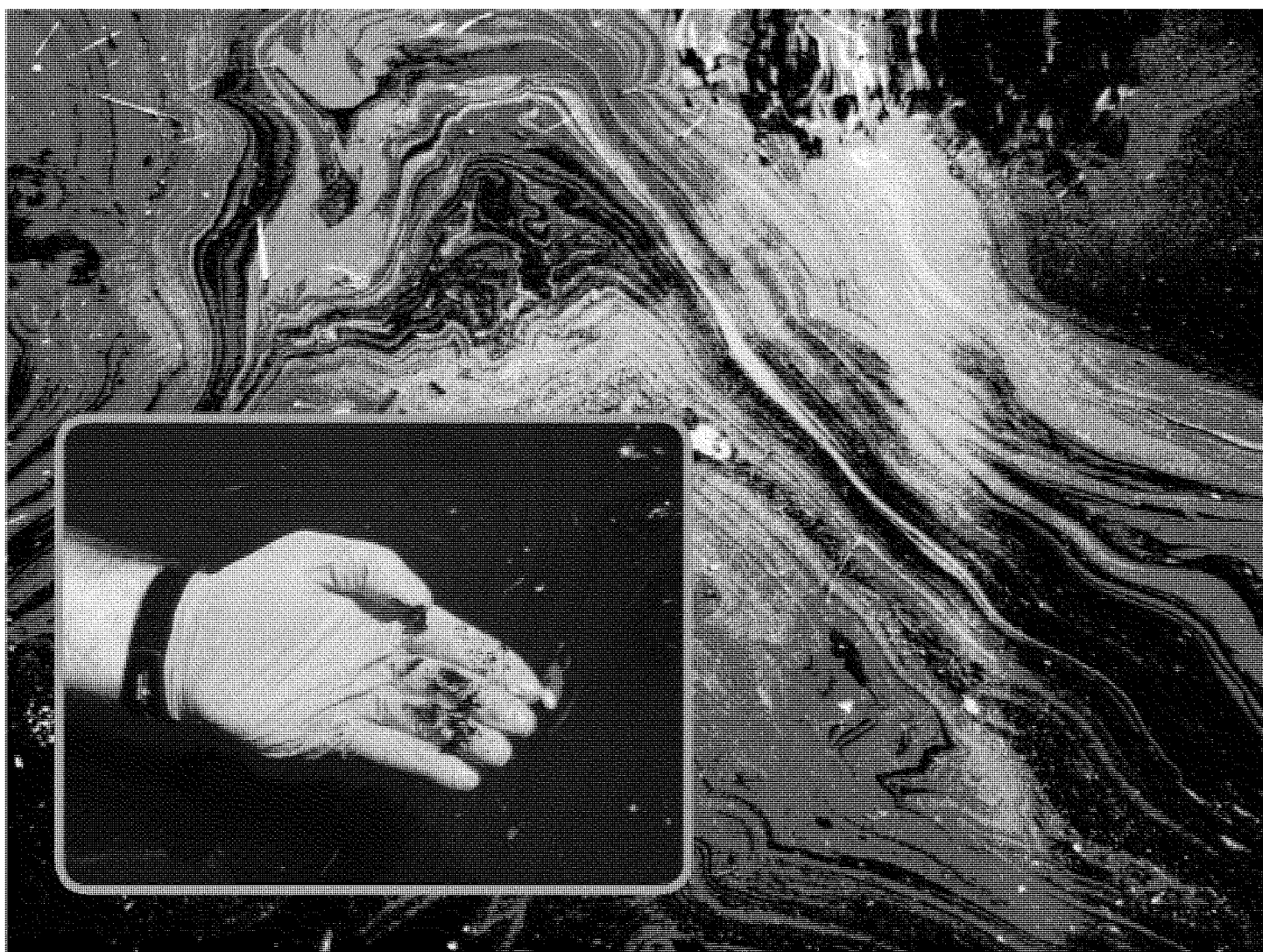
8505 Research Way

Middleton, WI 53562

office phone: 608-821-3818; cell 608-692-4891

email: fafitzpa@usgs.gov

On Wed, Sep 24, 2014 at 6:46 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hello Faith, I am curious if you have asked Ed to review – or is he a coauthor? Can you provide the abstract to the paper so that I can determine if I'm the best technical reviewer for it?

Thanks,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Fitzpatrick, Faith [mailto:fafitzpa@usgs.gov]
Sent: Tuesday, September 23, 2014 5:52 PM
To: Conmy, Robyn
Subject: Colleague review of USGS report "Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments--Review of the Science and Future Research Needs"

Hi Robyn, Would you have a the time/interest in reviewing the above named report on oil-particle aggregates? It is one of the background papers we are writing from the Kalamazoo River oil spill. It is ready for review. I'd need comments back in two weeks if possible. The report is 46 pages with 6 figures and a couple of small tables. Let me know what you think and I'll send you the

draft report if it sounds good. Or please forward on to someone else that you think might be good. Maybe Jim Weaver or Joe Schubauer-Berigan. But thought I'd start with you. Hope all is going good with you. Thanks, Faith

Faith Fitzpatrick, Ph.D.

Research Hydrologist (Fluvial Geomorphology)

USGS WI Water Science Center

8505 Research Way

Middleton, WI 53562

office phone: 608-821-3818; cell 608-692-4891

email: fafitzpa@usgs.gov

Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments— Review of the Science and Future Science Needs

Open-File Report 2015–1076

Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments—Review of the Science and Future Science Needs

By Faith A. Fitzpatrick, Michel C. Boufadel, Rex Johnson, Kenneth Lee, Thomas P. Graan, Adriana C. Bejarano, Zhenduo Zhu, David Waterman, Daniel M. Capone, Earl Hayter, Stephen K. Hamilton, Timothy Dekker, Marcelo H. Garcia, and Jacob S. Hassan

Open-File Report 2015–1076

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
Sally Jewell, Secretary

U.S. Geological Survey
Suzette Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2015

Contents

Figures

Tables

Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
Length		
micrometer (μm)	0.000039	inch (in.)
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square meter (m^2)	0.0002471	acre
square kilometer (km^2)	247.1	acre
square centimeter (cm^2)	0.001076	square foot (ft^2)
square meter (m^2)	10.76	square foot (ft^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
liters (l)	0.0063	Barrel (petroleum, 1 barrel = 42 gal)
liters (l)	0.2642	gallon (gal)
cubic meter (m^3)	6.290	barrel (petroleum, 1 barrel = 42 gal)
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter (m^3)	1.308	cubic yard (yd^3)
Flow rate		
meter per second (m/s)	3.281	foot per second (ft/s)
cubic meter per second (m^3/s)	35.31	cubic feet per second (ft^3/s)
Density		
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot (lb/ft^3)
Stress		
pascal (Pa)	0.000145	pound per square inch (psi)
Dynamic viscosity		
centipoise (cP)	2.42	pound/foot-hour (lb/ft-hr)
Energy dissipation rate		
square meters per cubic second (m^2/s^3)	10.76	square feet per cubic second (ft^2/s^3)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F=(1.8×°C)+32

vi

Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments—Review of the Science and Future Science Needs

By Faith A. Fitzpatrick[1], Michel C. Boufadel[2], Rex Johnson[3], Kenneth Lee[4], Thomas P. Graan[5], Adriana C. Bejarano[6], Zhenduo Zhu[7], David Waterman[7], Daniel M. Capone[8], Earl Hayter[9], Stephen K. Hamilton[10], Timothy Dekker[11], Marcelo H. Garcia[7], Jacob S. Hassan[12]

Abstract

Oil-particle interactions and oil submergence are of much interest to oil spill responders and scientists, especially as transportation of light and heavy crude oils increases in North America's coastal marine and freshwater environments. This report contains an up-to-date review of the state of the science for oil-particle aggregates (OPAs), in terms of their formation and stability which may alter the transport, fate, and toxicity of the residual oil and, hence, its level of ecological risk. Operational considerations—detection, containment, and recovery—are discussed.

Although much is known about oil-particle interactions in coastal marine environments, there remains a need for additional science on methods to detect and quantify the presence of OPAs and to understand their effects on containment and recovery of oil spilled under various temperature regimes and in different aquatic habitats including freshwater environments.

Introduction

Suspended particles affect the fate and transport of spilled oil in aquatic environments (Muschenheim and Lee, 2002; Owens and Lee, 2003; Khelifa and others, 2005a, b, c; Sun and Zheng, 2009; Gong and others, 2013), such as rivers and floodplains, shorelines and beaches along lakes and oceans, coastal and riparian wetlands, and deeper waters of oceans and lakes. The manner in which oil interacts with particles and its eventual transport and fate depend on the physical properties of the oil and the particles, as well as environmental conditions including the geomorphic setting, weather, currents, and vertical mixing of the water column (Lee, and others, 2011a; Lee and others, 2002) (fig. 1).

Combinations of oil and particles have various names, including clay-oil flocculation (Bragg and Yang, 1995), oil-mineral aggregates (Lee and others, 1998) and oil-suspended sediment-aggregates (Khelifa and others, 2002) depending on the type of particle involved in the interaction. The term oil-particle aggregate (OPA) is used in this report because it is the more generic term that includes a wider range of particles containing both mineral sediment and organic matter in association with oil that may be retained in suspension and (or) settled out.

[1]U.S. Geological Survey Wisconsin Water Science Center, [2]New Jersey Institute of Technology, [3]Global Remediation Technologies, Inc., [4]Commonwealth Scientific Industrial Research Organization (CSIRO), [5]Weston Solutions, Inc., [6]Research Planning, Inc., [7]University of Illinois Ven Te Chow Hydrosystems Laboratory, [8]Mannik Smith Group, [9]U.S. Army Corps of Engineers, Engineer Research and Development Center, [10]Michigan State University, [11]LimnoTech, Inc. [12]U.S. Environmental Protection Agency
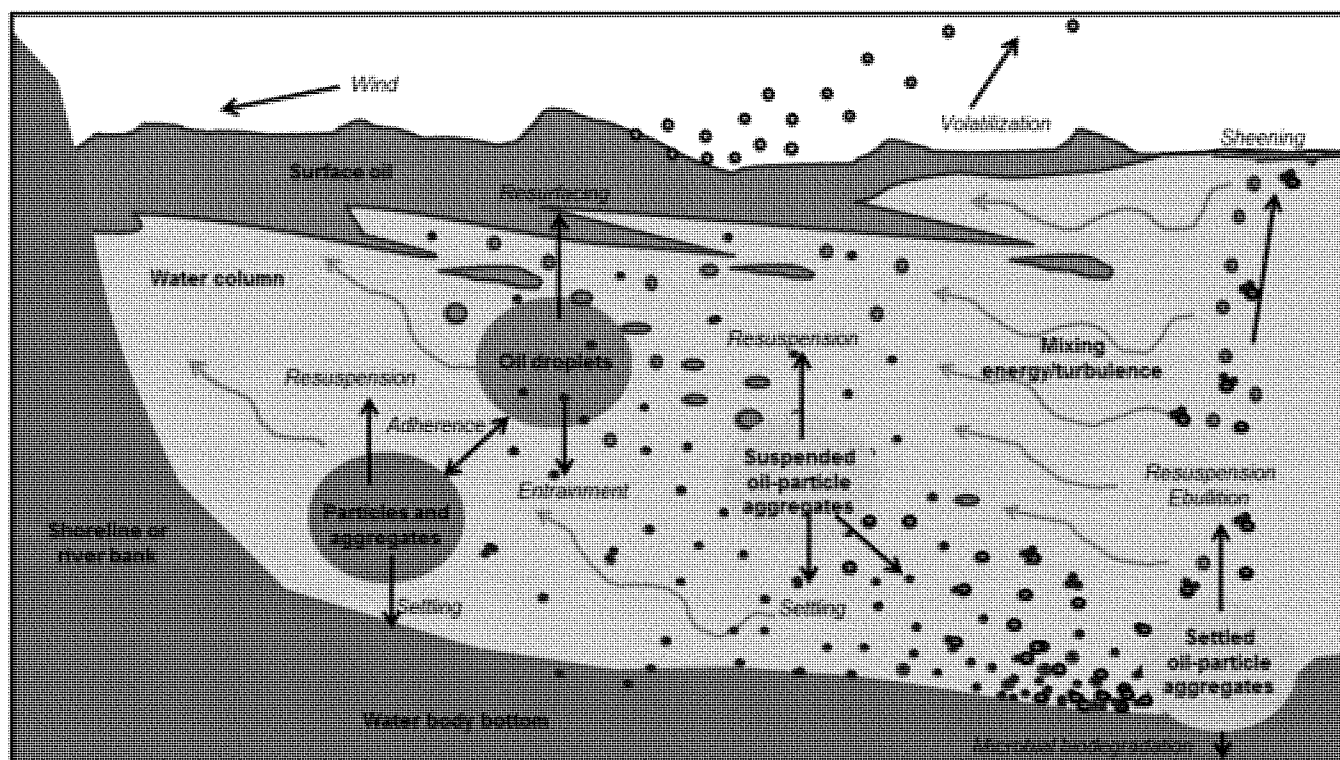
1

Figure 1. Simplified diagram of the processes and mechanisms leading to oil-particle aggregate formation and breakup in marine and freshwater environments. (modified from Environment Canada, 2013; OPA, oil-particle aggregate).

Traditional clean-up methods based on physical recovery of oil slicks on surface waters, such as booming and skimming, are ineffective for spilled oil once it submerges. Observations of OPA formation associated with the transfer of oil to the benthic environment (Lee, 2002; Payne and others, 2003; Sterling and others, 2005; Passow and others, 2012) have provided the justification for additional scientific studies to understand the processes and characteristics associated with OPA formation and their transport and fate. Results from additional studies will likely influence oil spill response contingency planning and spill response operations that include methodologies for detection, monitoring, recovery, and containment (Bandara and others, 2011; Environment Canada, 2013; Dollhopf and others, 2014; Hansen, 2014).

OPA formation has been correlated with the removal of oil stranded within sediments in freshwater and marine environments by both natural recovery (natural attenuation) and active remediation procedures (the addition of suspended particulate material in the presence of turbulent mixing energy) (Bragg and Yang, 1995; Lee and others, 1996; 1997; Wood and others, 1997; Lee, 2002; Lee and others, 2002; Owens and Lee, 2003). Lee and others (1997; 2003a) note that OPA formation accelerated the removal of stranded oil within the intertidal/surf zone by reducing the adhesive properties of the oil and the tendency of dispersed droplets stabilized by mineral fines to re-coalesce. Thus, either formed naturally or enhanced with addition of clay minerals, the relatively stable OPAs are dispersed more easily in the water column, potentially reducing the oil to concentrations below toxicity threshold limits (Lee and others, 2003a; Lee and others, 2003b) and making the oil more available for biodegradation (Weise and others, 1999; Lee and others, 1996; Lee and others, 1997; Lee and Merlin, 1999; Owen and Lee, 2003). Like chemical dispersants, the exposure pathway is altered

2

from water surfaces and shorelines to the water column, which transfers the toxicity risks from water fowl and shoreline organisms to planktonic, open water, and benthic species (Venosa and others, 2014).

Submergence can happen to light and heavy oils after they bind to relatively small amounts of particles (mineral sediment or organic matter). This can occur in suspension or while the oil moves along the bottom of a water body, bank, or coastline (Lee and others, 1985; Lee, 2002; Cloutier and others, 2003). The behavior of bitumen from the Canadian tar sands (usually more dense and viscous than traditional heavy oil), and particularly its interaction with particles leading to eventual submergence and accumulation of OPAs in sediments, has recently become a topic of much interest because of the 2010 Enbridge Line 6B pipeline release into the Kalamazoo River when more than 3.2 million liters of diluted bitumen were released into the Kalamazoo River in Michigan (Dollhopf and others, 2011). Response operations for that release began with conventional recovery techniques for floating oil and recovered about 2.9 million liters; however, submerged oil became the focus approximately 1 month into the cleanup and remained the focus through the summer of 2014 (Enbridge Energy, L.P., 2010; Dollhopf and others, 2014). Given the timely research efforts pertaining to the Canada Northern Gateway proposed pipeline, recent studies provided insights on the buoyancy (King and others, 2014), interaction with mineral fines (King and others, 2015), and the ultimate fate of OPAs formed from bitumen (Environment Canada, 2013).

Light crude oil can interact with particles along rivers, as indicated by the 2013 derailment, explosion, and spill of light crude oil in Lac-Mégantic, Quebec when an estimated 100,000 liters of oil spilled into the Chaudière River. A management plan by the Government of Quebec was developed that included recommendations for cleanup of river bottom sediment contaminated with hydrocarbons (Gouvernement du Quebec, Depot Legal, 2014). Laboratory tests at Louisiana State University using E2MS 303 oil from the February 2014 spill of Bakken crude from a barge collision into the lower Mississippi River indicate that the "oil will quickly adhere to suspended solids in the water column, forming unstable emulsions" (Doelling and others, 2014).

More than 15 years ago, before the emergence of concerns about increased pipeline transport of diluted bitumen, the National Coastal Research Council (on behalf of the U.S. Coast Guard) published "Spills of Nonfloating Oils: Risk and Response," a report that included specific recommendations for detection, monitoring, modeling, and recovery of submerged oil, mainly in marine environments (National Research Council, 1999). These recommendations were further tabulated into science needs for detection and monitoring, fate and transport, containment and recovery, and effects and restoration and included specific mention of OPAs (Coastal Response Research Center, 2007). Some areas of science support included developing better sensors to detect OPAs, mapping the extent of OPAs, and determining future resuspension and remobilization of OPAs in bottom sediment. The Coastal Response Research Center (2007) noted that improved characterization of the size, composition, and distribution of particles would enable better forecasting, observation, understanding, and hind casting of OPA behavior for a range of ecological and geomorphic settings.

Fisheries and Oceans Canada has been conducting oil-particle interactions studies with oil and chemically dispersed oils since the mid-1980s. An oil-particle interactions workshop was organized in 2000, and a compendium of papers appeared in the Spill Science and Technology Bulletin in 2003 and 2004 (Lee and Jarvis, 2004). These publications formed the basis for a quickly growing body of literature on the topic of OPAs in both marine and freshwater environments.

Because oil transportation in North America increased greatly on rails, through pipelines, and on barges and vessels as a result of the increased production of Bakken crude in the Williston Basin, North Dakota, and bitumen in the western provinces of Canada (Frittelli and others, 2014; Association of American Railroads, 2014; Committee for a Study of Pipeline Transportation of Diluted Bitumen,

3

2013), more attention is being given to submerged oil detection and response techniques in marine and freshwater environments (Coastal Response Research Center, 2007; Hansen, 2014). It is clear that more science is needed on the formation, settling, resuspension, and toxicity of OPAs, and the manner in which these properties vary depending on the nature of the oil and the characteristics of the aquatic environment it enters. Quantification of residual oil following spill response operations needs to account for the fraction of oil associated with suspended/settled particulate material.

Purpose and Scope

The purpose of this report is to describe the state of the science concerning OPAs—their formation, transport, settling, resuspension, and breakup in a variety of geomorphic environments including coastal marine, deep ocean, freshwater lacustrine (Great Lakes), and riverine, and brackish river mouths and harbors. The report contains a synthesis and review of available literature on OPAs from laboratory, experimental tank and flume studies, and some large-scale field experiments. Ongoing studies are described and needs for continuing investigation and new science on OPAs are listed.

Review of the Science

The U.S. Geological Survey (USGS) mission is to provide reliable scientific information to describe and understand the Earth; minimize loss of life and property from natural disasters; manage water, biological, energy, and mineral resources; and enhance and protect our quality of life. That mission has involved the USGS in providing science support for oil spill recovery. This review of the science on oil-particle interactions was motivated by questions that have arisen during oil spill response of the Enbridge Line 6B spill in Marshall, Michigan. However, the review is holistic in the sense that it incorporates spills of oils with various properties in freshwater and marine environments, as a result of concerns about spills from the rising quantities of crude oil produced and transported across the Nation. The following questions helped to form the major sections included in this review:

- ☐ What environmental conditions lead to the formation of OPAs?
- ☐ What is the effectiveness of adding particles to an oil spill for physical dispersion of oil as a spill countermeasure?
- ☐ What is the long-term fate and transport of OPAs?
- ☐ What are the ecological implications (fate and effects) of OPAs?
- ☐ Are there special circumstances for OPAs in cold climates for use as a spill countermeasure or for recovery in icy water?
- ☐ What are the operational considerations for recovery of OPAs?

Formation of Oil-Particle Aggregates

Formation of OPAs happens naturally when oil and suspended particles mix in turbulent water (Lee, 2002; Muschenheim and Lee, 2002; Owens and Lee, 2003; Khelifa and others, 2005a; Sun and Zheng, 2009; Gong and others, 2013). An understanding of the exact mechanisms of OPA formation comes mainly from the use of laboratory shaker and wave tanks, including those at the Bedford Institute of Oceanography, Dartmouth, Nova Scotia (Center of Offshore Oil and Gas Environmental Research, 2004), and flume experiments. Results from wave tank and laboratory shaker experiments provide empirical data for models of OPA formation and breakup (Stoffyn-Egli and Lee, 2002; Li and others, 2007; Ma and others, 2008; Wang and others, 2011). However, field observations and data from

4

assessment and monitoring activities at spill sites yield information on the timing and range of environmental conditions under which OPAs have formed (Niu and others, 2011).

Major factors affecting the formation of OPA are (1) quantity and viscosity of the oil, interfacial tension of oil-water, and chemical composition of the oil; (2) quantity, type, and surface properties of the particles; (3) magnitude and variability in physical energy of the aquatic environment; (4) temperature; and (5) salinity (Lee, 2002; Khelifa and others, 2002; Payne and others, 2003). Recent tests have focused on the highly viscous diluted bitumen (dilbit) product (Zhao and others, 2014a). In spills of heavy crude oil, particularly bitumen, freshwater environments with fine-grained sediment in the water column and bottom, abundant sunlight, warm temperatures, and strong currents and turbulence create a high potential for oil submerging and ultimately being deposited in the sediments (Silliman, 2014).

The first step to forming OPAs lies with the initial breakup of a slick of oil into oil droplets. Once spilled into a water body with turbulence created by waves or currents, floating oil can break up into droplets and reach a stable droplet size distribution (DSD) relatively quickly, perhaps in minutes to tens of minutes (Zhao and others, 2014b). Smaller droplets are generated when the interfacial tension of oil-water is small and (or) the oil viscosity is small. The interfacial tension of oil-water is more or less constant in the absence of surfactants. However, oil viscosity can increase by orders of magnitude among different types and temperatures of oils (fig. 2). For example, the viscosity of a heavy crude oil or bitumen is at least 1,000 times that of light crude such as a product from the Alaska North Slope or Bakken Formation oil (http://www.etc-cte.ec.gc.ca/databases/oilproperties/Default.aspx). Figure 2 contains a summary of American Petroleum Institute (API) gravity and viscosity for the major categories of crude oil (American Petroleum Institute, 2011). Crude oil densities are usually measured in terms of degrees API gravity. A higher API gravity corresponds with lighter density, with freshwater at 10 degrees API. Crude oils are generally further categorized by their type of hydrocarbon base (paraffinic or naphthenic) and sulfur content (high–sour, low–sweet).

For the common numerical models for the evolution of the DSD, it has been assumed that the interfacial tension is the only force resisting the breakup of droplets (Prince and Blanch, 1990; Tsouris and Tavlarides, 1994), which is not the case for high viscosity oils or for situations when surfactants (in the form of chemical dispersants) are used (Wang and Calabrese, 1986). Alternatively, Delvigne and Sweeney (1988) developed an expression that predicts dispersion, which is based on oil viscosity without any information on the oil-water interfacial tension. Thus, the Delvigne and Sweeney (1988) formula cannot be relied upon to account for the reduction in the interfacial tension when dispersants are used. Recently, Zhao and others (2014b) developed a comprehensive model that accounts for resistance to breakup from both interfacial tension and viscosity of the oil. This model is called VDROP to stress the important role of viscosity. The DSD depends also on the mixing energy, namely the dissipation rate of kinetic energy (National Research Council, 2005; Kaku and others, 2006). Thus, high mixing energy promotes the breakup of droplets (fig. 1). In addition, dilution (as oil mixes with a larger volume of water away from the source) increases the distance between oil droplets and thus minimizes the probability of collision and subsequently the coalescence of oil droplets into larger droplets.
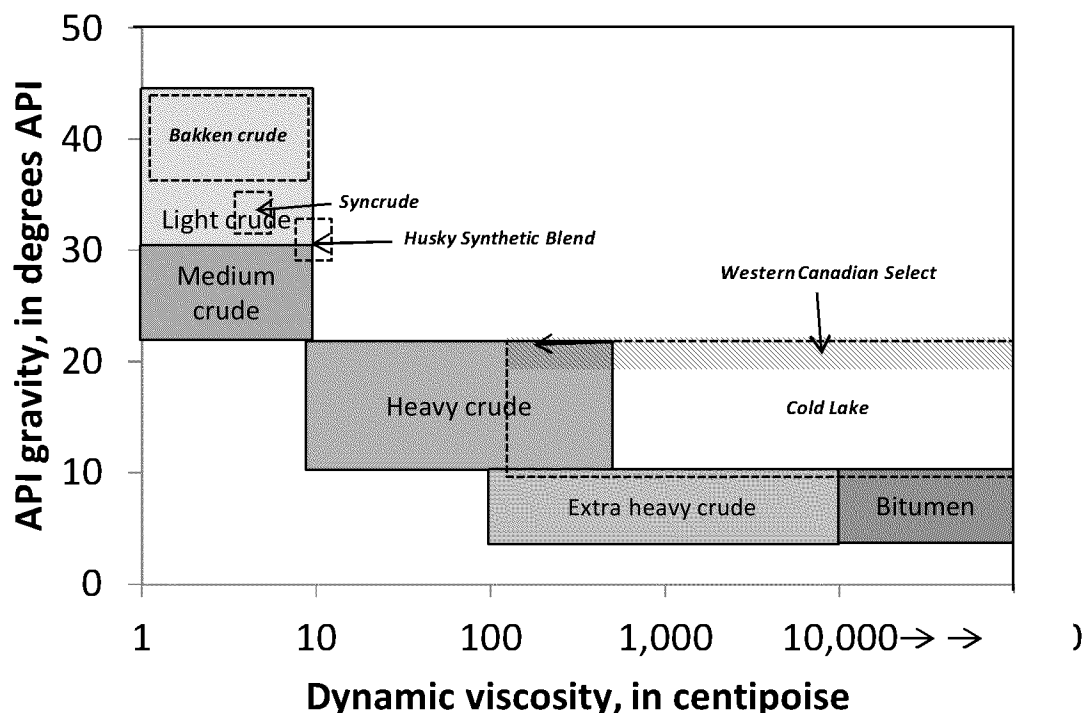
5

Figure 2. Summary of American Petroleum Institute (API) gravities and dynamic viscosities (at approximately 10-20 degrees Celsius) for major categories of crude oil types and bitumen/oil sands. Overlays are of example crude oils commonly transported in North America. Data summarized from Attanasi and Meyer (2007), American Petroleum Institute (2011), Sia Partners Energy Outlook (2011), Environment Canada's Oil Properties Web Site http://www.etc-cte.ec.gc.ca/databases/oilproperties/Default.aspx, Andrews (2014), Doelling and others (2014), Crude Quality, Inc. (2014); and Enbridge Energy Partners, L.P. (2013).

The size of the oil droplet is a very important factor in the transport and fate of the oil and its interaction with particles. Because large droplets have higher buoyancy than smaller droplets, they tend to float to the water surface, whereas smaller droplets could be driven more easily in the water column as a result of mixing energy (Boufadel and others, 2007). Smaller droplets also have a larger specific area than large droplets, which would enhance dissolution and microbial biodegradation (Lee and others, 1997; Lee and Merlin, 1999; Reddy and others, 2012; Geng and others, 2013).

When particles are attached to oil droplets, they form a type of barrier around the droplet that keeps it from coalescing with other oil droplets (Khelifa and others, 2005a). Droplets with particles result in three main features that contribute to the eventual fate and submergence of droplets: (1) OPA-enhanced stability of the oil droplets that limits coalescence; (2) increased specific density of coated droplets which causes dispersion into a water body and possible settling; and, (3) enhanced microbial degradation.

The actual attachment of oil droplets to particles depends on the viscosity and adhesion properties of the oil droplet and the surface area of the particles, as well as salinity of the water body (Lee, 2002; Khelifa and others, 2005a). There is evidence that salinity increases the formation of OPAs as a result of the reduction of the thickness of the double layer with increased ionic strength of water (Clark, 2009). However, OPA was also observed to form in freshwater (Lee, 2002; Lee and others, 2002). If the droplet size distribution of oil has not reached a steady state prior to interaction with the

6

particles, the interaction would affect the breakage mechanism of oil droplets. The reduction in the net interfacial tension resulting from attachment of particles would make the oil viscosity the main force resisting oil breakup. In such a case, a model that accounts for oil viscosity in resisting breakup is needed, such as VDROP (Zhao and others, 2014b).

Particle size, amount, and type are important to the formation of OPAs. Clay-sized mineral particles are effective at forming OPAs, especially if the particles are present in large concentrations (Lee and others, 1998; Lee, 2002). However, most natural waters have a range of particle sizes or at least bimodal distributions, and natural particle-size distributions also may vary with the amount of mixing resulting from waves or currents (Boufadel and others, 2007). The particles may be smaller than the oil droplet and form a coating, or they may be larger or the same size for an aggregate. In either droplet type (fig. 3A), the attachment of the oil droplet and particle reduces the interfacial tension of the OPA with the water, and thus the particles have an overall effect similar to surfactants (Lee, 2002). Oil also may attach to mineral or organic matter (Lee, 2002). Phytoplankton can readily form oil-organic aggregates in laboratory tests (Lee and others, 1985). Particle concentrations can be relatively low and still form OPAs (Lee and Stoffyn-Egli, 2001; Rymell, 2009); Khelifa and others (2002) note that, in laboratory shaker experiments with seawater, mineral concentrations as low as 100 milligrams per liter (mg/L) and moderate shaking resulted in OPA formation with various types of oil.

The shape and makeup of OPAs can take multiple forms. Methods used to study the shape and makeup of OPAs, which are generally less than 1 millimeter (mm), involve instrumentation such as combined transmitted light/ultraviolet (UV) light epi-fluorescence microscopy, confocal scanning laser microscopy, and environmental scanning electron microscopy (Stoffy-Egli and Lee, 2002; Lee and others, 2012). The most common forms of OPAs involve a spherical oil droplet surrounded by particles or multiple spherical droplets in a particle aggregate (Bragg and Owens, 1994; Stoffyn-Egli and Lee, 2002; Khelifa and others, 2005a; Zhang and others, 2010; Lee and others, 2012) (fig. 3A). Spherical shaped OPA indicate that the spilled oil formed droplets before forming aggregates, as described in the previous paragraphs. Stoffyn-Egli and Lee (2002) also found two other types of aggregates in laboratory experiments—solid and flake types (figs. 3B and 3C)—that do not necessarily form from dispersed droplets. These additional types are distinguished in that the oil takes on more of the form of the particle or mineral, and the flake type is distinguished by having folds or rolls in a dendritic or feather shape. For all types, the combination of oil and particles can result in a range of specific gravities that are usually similar to, or heavier than, water; thus OPAs can be floating, neutrally buoyant (in suspension), or negatively buoyant (submerging or settling) (Stoffyn-Egli and Lee, 2002). Sometimes the mineral makeup of particles determines their buoyancy, and Omotoso and others (2002) found that low-viscosity oils formed negatively buoyant OPAs with hydrophilic minerals (having a strong affinity for water) but formed positively buoyant OPAs with calcite minerals. Lastly oil-particle interactions can be enhanced by colloidal mechanisms of coagulation of ions (Lee and Stoffy-Egli, 2001), as well as biological activity associated with bacteria and phytoplankton (Passow and others, 2012).

Laboratory simulations of the formation of OPAs in a brackish (salinity of 1.5 parts per thousand) high-energy riverine environment (Rio Desaguadero) were done by mixing sediment-laden water and heavy crude oil from the 2000 OSSA II pipeline spill into the Rio Desguadero in the Bolivian Altiplano (Lee and others, 2001; 2002). In this spill, a missing oil fraction of 27–37 percent was not recovered; presumably it succumbed to from oil dispersion and enhanced biodegradation caused by the formation of OPAs. The river sediment was rich in smectite clay minerals, which have an affinity for attracting or adsorbing water molecules. Also, the river was in flood stage, with velocities of 2.5 meters per second (m/s) and depths of less than 3 meters (m). Both of these factors may have enhanced OPA formation. The laboratory experiments, which were run at water temperatures of 20–22 degrees Celsius

7

(°C), showed that the amount of OPA formation increased with increasing salinity, which is known to cause flocculation of clays. With a combination of fresh OSSA II oil (diluted with a kerosene-range petroleum product), Rio Desaguadero sediment, and solutions using natural seawater and dilution to obtain salinities of 0.35, 0.7, 1.2, 3.5, and 35 parts per thousand (ppt), OPA formation increased with increasing salinity, and at 35 ppt almost all of the oil was taken up in OPA formation (fig. 4). In contrast, a minimal amount of oil was present as OPAs with fresh oil, distilled water, and river sediment, but when the brackish river water was used (1.5 ppt salinity), about 25 percent of the fresh oil formed OPAs.
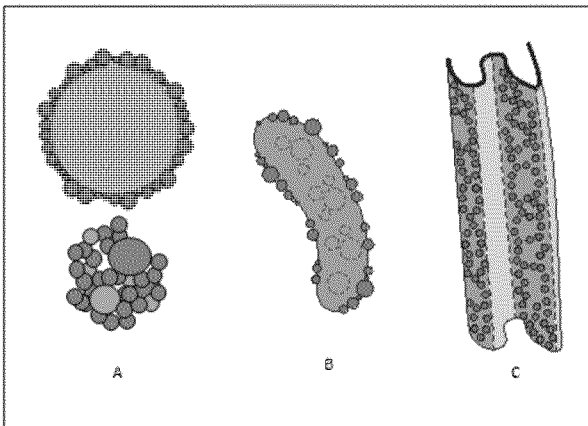
Figure 3. Types of oil-particle aggregates: A, single and multiple droplet aggregate, B, solid aggregate of large, usually elongated mass of oil with interior particles (dashed blue circles), and C, flake aggregate of thin membranes of clay aggregates that incorporate oil and fold up (modified from Stoffyn-Egli and Lee, 2002). Blue color represents particles and yellow represents oil.
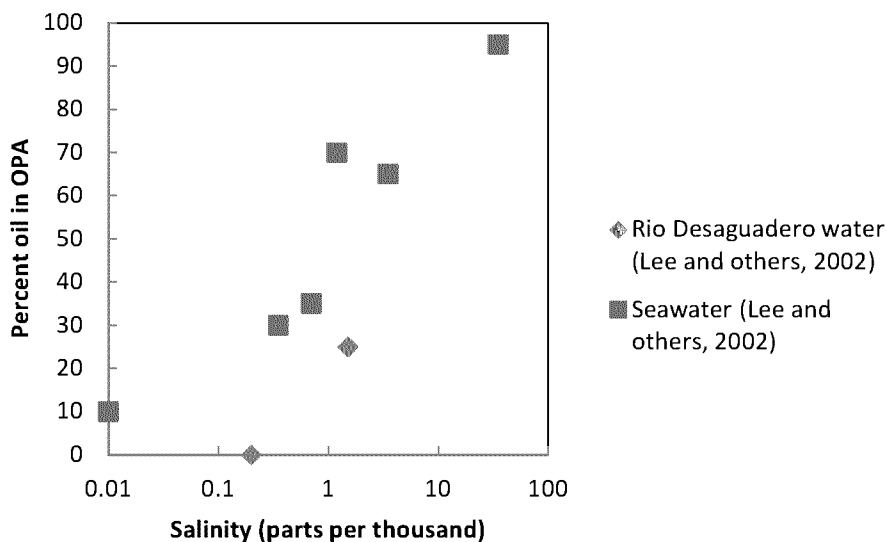
Figure 4. Salinity in relation to the percent of oil in oil-particle aggregates (OPAs) from laboratory shaker tests of diluted heavy crude oil form the 2000 OSSA II spill into the Rio Desaguadero in Bolivia and its smectite-rich sediment. (Graph replotted from Lee and others, 2002).

8

Natural formation and submergence of OPAs occurred in the freshwater, low-gradient environment of the Kalamazoo River after the 2010 Enbridge Line 6B pipeline spill of diluted bitumen into Talmadge Creek, a tributary of the Kalamazoo River near Marshall, Michigan (Dollhopf and others, 2014). The diluent of natural gas condensate (which is used as a solvent in the mixture) volatilized and submergence of the bitumen occurred within a few weeks following the spill (Dollhopf and Durno, 2011; Lee and others, 2012). On the basis of laboratory tests of Cold Lake Blend by Belore (2010) and in an outdoor flume by King and others (2014), the density of the spilled bitumen (mainly Cold Lake Blend) was likely between 0.93 and 0.936 grams per cubic centimeter (g/cm^3) with diluent and 0.981 g/cm^3 after the diluent evaporated. The dynamic viscosity of the Cold Lake Blend in the Belore (2010) laboratory tests ranged from approximately 400 centipoise (cP) with diluent to more than 14,500 cP after evaporation of the diluent. Both the works of Belore (2010) and King and others (2014) were conducted at approximately 15°C.

Some features of the Kalamazoo River likely enhanced the formation, resuspension, and deposition of OPAs. The Enbridge Line 6B pipeline release happened during a flood on the Kalamazoo River with an exceedance probability of 4 percent (for example, a 25-year event) (Hoard and others, 2010) and with a mean velocity of about 1.1 m/s and a mean depth of 1.2 m near the USGS streamgage at Marshall, Michigan (04103500). On the basis of later measurements of suspended sediment at the Marshall streamgage, it can be inferred that, at the time of the spill, the river had relatively low suspended sediment concentrations (less than 100 mg/L) (fig. 5) with suspended particle sizes mainly in the silt-sized range (65–75 percent) (fig. 6). Water temperatures were warm, in the range of 23–25 ° C (Stephen Hamilton, Michigan State University, written commun., 2014). Floodwater increased turbulence in river flows and increased the presence of suspended particulate matter. Additional mixing from flows over two dams may also have played a role, although OPAs and submerged oil accumulated in the first 5 kilometers (km) of river length, between the spill source and the first dam. Aggressive sediment agitation techniques (raking, flushing, aeration, and skimming the river bottom physically or with water jets) were conducted in 2011 to liberate submerged oil as recoverable sheen in 2011 (Enbridge Energy L.P., 2011b; Dollhopf and others, 2014), potentially contributing to further OPA formation and transport of OPAs to downstream reaches (Lee and others, 2012). Lee and others (2012) found that oil from the pipeline spill readily formed OPAs when mixed with Kalamazoo River sediment in laboratory tests (fig. 7).

Assuming that the fraction of spilled oil not recovered by conventional techniques was lost to submergence, the bitumen that submerged in the Kalamazoo River was greater than 300,000 liters, which is around 10 percent of the spilled oil. This is based on the Enbridge Energy, L.P., reported spilled amount of 3.2 million liters and recovered amount of 2.9 million liters after the first year (U.S. Environmental Protection Agency, 2011). Although the volume of oil released and remaining in the river are not finalized at the time of this writing (January 2015), the estimated percentage is similar to that found by Lee and others (2002) for distilled water and brackish water of the Rio Desaguadero (fig. 4). Even though OPA formation in freshwater may be less than that in seawater, the persistent residual submerged oil and oiled sediment in the Kalamazoo River resulted in a protracted cleanup that ultimately required dredging and has accounted for a major share of the cleanup costs, which have surpassed $1.2 billion (Dollhopf and others, 2014).

9
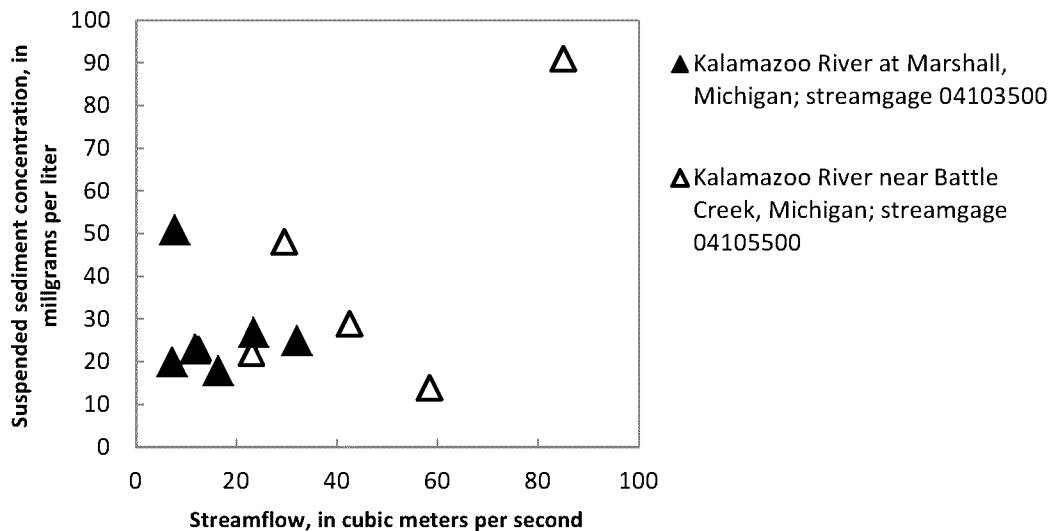
Figure 5. Streamflow in relation to suspended sediment concentration in the Kalamazoo River, Michigan, August 2012-March 2014. Streamflow during the pipeline release on July 28, 2010, during a receding flood event with a 4-percent exceedance probability, was about 34 cubic meters per second (m³/s) at Marshall, Michigan and 85 m³/s near Battle Creek, Michigan. The Kalamazoo River is generally a suspended sediment supply -limited system, shown by the overall low concentrations over the entire flow range at both streamgages.
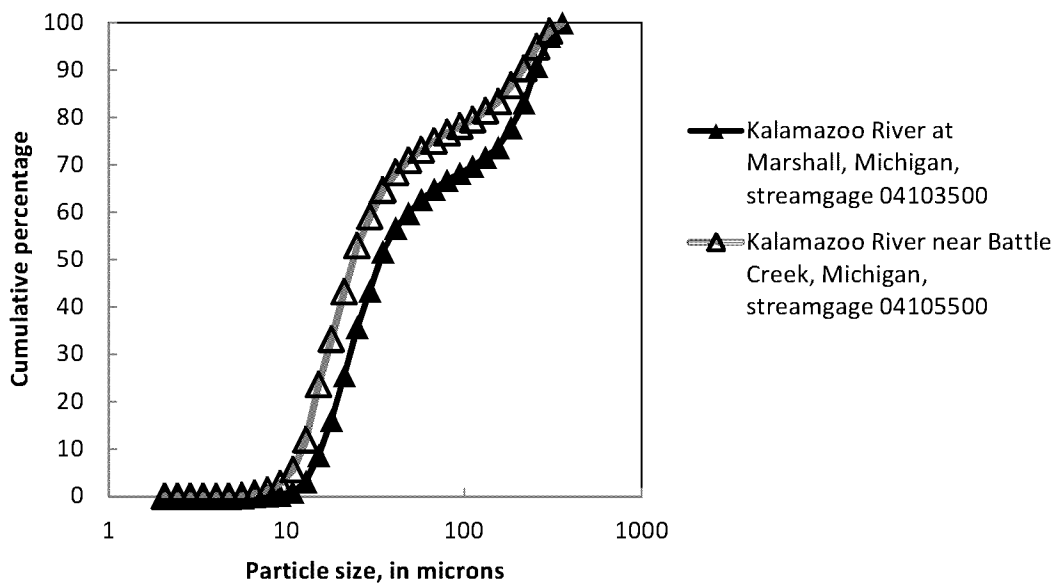
Figure 6. Cumulative particle-size distribution for suspended sediment collected April 22, 2013, during flows of 32 cubic meters per second (m³/s) at Marshall, Michigan, and 85 m³/s near Battle Creek, Michigan. Most of the suspended sediment was in the silt-size class—about 65 percent at Marshall and 75 percent near Battle Creek. Samples analyzed with portable laser in-situ scattering and transmissiometry.

10
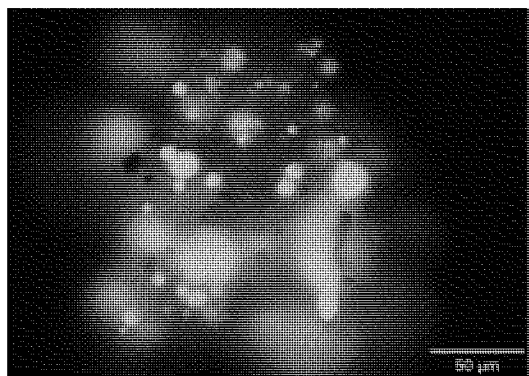
Figure 7. Kalamazoo River sediment spiked with weathered source oil after 48 hours, under ultraviolet-epifluorescence microscopy at 320 times magnification. (from Lee and others, 2012).

Some additional features of the Kalamazoo River may have been important factors in OPA formation, transport, and deposition. The floodplain of the Kalamazoo River has abundant wetlands, thus suspended and bottom sediments have relatively high organic matter content, on the order of 20 percent or more. The river is wide (width/depth ratios of 40) and has an average gradient of 0.06 percent in the spill-affected reach. Deposition of OPAs occurred along channel margins, backwaters, side channels, and oxbows, and in impoundments throughout the entire 61- km stretch of the river affected by the oil spill. Surveys over time provided evidence for resuspension and resettling of OPAs in downstream areas, presumably during post spill floods (Dollhopf and others, 2014).

Oil-Particle Aggregates as a Natural Physical Dispersant

Enhancing physical dispersion of spilled oil through the addition of particulate matter is one of several techniques that have been used for spill cleanup and to prevent oiling of marine coastal areas (Zhang and others, 2010). The oil would be dispersed into small droplets by turbulent mixing from waves or currents and subsequently mixed with mineral and organic particles in the water column. The aggregation of the oil with particles to form OPAs and their subsequent physical dispersion by natural processes would reduce the bioavailability and toxicity of the residual oil to aquatic organisms in the vicinity of the spill. Furthermore, as the activity of oil degrading bacteria is focused at the oil water interface, the formation of small oil droplets enhances microbial biodegradation (Lee and others, 2002; 2009). Petroleum hydrocarbons are not new to the environment because of natural sources such as seepage from oil bearing rocks and biological production by plants and animals. Thus, indigenous oil degrading bacteria are readily available in many aquatic ecosystems (Atlas and Hazen, 2011).

OPA formation has been reported to be a significant contributor to the natural cleansing mechanisms observed during the Baffin Island Oil Spill (BIOS) project and recovery following the Exxon Valdez oil spill incident in 1989 (Bragg and Owens, 1994; Bragg and Yang, 1995). Studies have shown that microorganisms (namely bacteria and archea) within ocean floor sediments in the proximity of natural oil seep sites, such as Scott Inlet, Baffin Island, and the Gulf of Mexico have adapted to utilize oil droplets as a carbon and energy source (Grant and others, 1986; Atlas and Hazen, 2011). The current scientific consensus is that a considerable portion of the oil spilled in the Gulf of Mexico from the Deepwater Horizon incident has been degraded by indigenous bacteria (Atlas and Hazen, 2011; National Research Council, 2013). Considering the magnitude of the spill, Edward Owens (Polaris Applied Science, Inc., oral commun., 2014) has hypothesized that the volume of oil affecting the Gulf of Mexico shoreline was much less than expected, because of the interaction of dispersed oil and surface oil slicks with the naturally high concentration of particulate suspended material near the coast.

11

Boufadel et al. (2014) conducted a comparison between the DWH and the Exxon Valdez spills, and based on calibrated modeling, they estimated that around the same mass of oil reached the shorelines from the two spills (around 20,000 tons). But the percentages to the total mass of oil were around 5 percent and 50 percent for the DWH and Exxon Valdez, respectively. For the 1989 Exxon Valdez oil spill, much of the oil along shorelines was depleted (Atlas and Hazen, 2011), except in some beaches with anoxic conditions (Boufadel and others, 2010; Li and Boufadel, 2010).

With natural particulate matter readily available in a coastal marine or lacustrine environment, and especially along river systems, OPA formation must be considered a natural process that enhances the physical dispersion of oil. Indeed, expanding on this hypothesis, Lee and others (2009) suggested that active enhancement of OPA production as a "physical" means to promote oil dispersion, could be an alternative to the use of chemical dispersants that may be potentially toxic in their own right. However, prescribed sinking of spilled oil, or the use of sinking agents, is currently prohibited by U.S. Environmental Protection Agency (EPA) because of the potential risks of acute and chronic toxic effects on benthic organisms and possibly less biodegradation once the oil is deposited (U.S. Environmental Protection Agency, 1993; also 40 C.F.R. §§ 300.310(b), 300.910(e)).

Laboratory experiments have expanded on the knowledge base of the manner in which OPAs facilitate physical dispersion in both seawater and freshwater. For seawater, simulations of coastal environments by Li and others (2007) in wave tank experiments found that chemical dispersants and the addition of fine mineral particles, alone and in combination, enhanced the dispersion of light crude oil in the water column and increased the number of OPAs formed. Similarly, results from wave tank studies of light crude oil with seawater (Lee and others, 2008) indicate that chemical dispersants enhanced OPA formation by transferring oil from a slick floating on the water surface into oil droplets in the water column that more easily interacted with suspended particles. Zhang and others (2010) considered three crude oils (Mesa, Alaska North Slope, and Heidrun) with specific gravities from 0.8746 to 0.9058 g/cm^3 (at 22°C). They conducted laboratory experiments in seawater to evaluate the combined effects of three factors—chemical dispersants, mixing energy, and mineral types—on OPA formation. They also discussed the usage of OPA as a response technique. They found that hydrophobicity (aversion toward water), particle size, and specific surface area of minerals are key factors, which is consistent with other findings in the literature. Slightly hydrophobic particles enhanced formation of OPAs by promoting the attachment of mineral particles to oil. However, highly hydrophobic particles clumped together and did not interact with the oil. Therefore, there was an optimum range of hydrophobicity for maximum OPA formation. If minerals were hydrophilic, the OPAs were generally spherical. Hydrophobic minerals formed irregularly shaped OPAs. The OPAs were larger for hydrophobic particles than for hydrophilic minerals. Chemical dispersants when added became the overriding factor affecting OPA formation because of their stabilizing effect on oil droplets. High mixing energy enhanced dispersion of oil into the water column to form droplets and small-sized OPAs. The Zhang and others (2010) study concluded that in areas of low mixing energy, a chemical dispersant might be needed with a co-application of fine mineral particles to form OPAs.

Laboratory studies in freshwater using automated shaker tests of mixtures of kaolinite clay-sized particles and heavy and intermediate fuel oils (viscosities of 3,900 and 1,350 cP, respectively) were conducted by Perez and others (2014) to simulate of the interaction of oil slicks and suspended sediment in steep, turbulent rivers. Using a spectrophotometer for oil measurement, the amount of oil entrained by sediment was observed to be moderate for heavy fuel oils at wave heights of 2.5 and 7 cm and kaolinite concentrations of up to 16,000 parts per million (ppm). They predicted that a surface slick of 1,000 kg of IFO across a river width of 10 m would result in about 8 percent of the oil entrained in OPA over a 1 km length. However, there was a large variability in the data, and thus these results still need

12

confirmation of scaling factors using either large scale experiments or with computational fluid dynamics models.

Khelifa and others (2005b) and Niu and others (2010, 2011) developed predictive models to estimate the contribution of OPAs to the dispersal of spilled oil and their potential to cause secondary detrimental effects associated with physical inhibition (that is smothering of benthic organisms) or toxicity. Factors considered in these models include the calculation of the maximum size of droplets, prediction of oil droplet formation from a slick, prediction of sediment aggregate formation, and the calculation of the density of the resultant oil-sediment aggregate. Inputs to the models include environmental conditions, oil properties, and concentration and particle-size distribution of suspended sediment. In a model sensitivity analysis of five crude oils (Hibernia, Louisiana, Prudhoe Bay, Arabian Light, and Alaska North Slope), with a range of densities from 25 to 37 degrees API and dynamic viscosities from 8 to 68 cP, the kinetic energy dissipation rate was varied from 10^{-3} to 10^2 square meters per cubic second (m^2/s^3) with a sediment particle size of 3 micrometers ($\square$m) and concentration of 250 mg/L; the study showed that OPA formation is strongly dependent on the oil-water interfacial tension and kinetic energy dissipation rate. The OPA contribution to oil dispersion increased when energy dissipation rates were about 1 watt/kg or higher. High turbulence in surf zones or in rivers should therefore be conducive to higher rates of OPA formation.

Transport and Fate of Oil-Particle Aggregates

As described in the section "Oil-Particle Aggregates as a Natural Physical Dispersant", formation of OPAs changes the fate and transport of oil by potentially changing its rate of horizontal and vertical transport, and biodegradation and levels of bioavailability, which ultimately influence the ecological effects of OPAs. Because of the range of variance in physical, chemical, and biological conditions between sites (for example, types of suspended particulate organic/inorganic material, type of oil, mixing energy) differences in the transport and fate have been observed between marine and freshwater environments. In the coastal marine environment, the formation of OPAs has been found to improve removal of stranded oil from low-energy intertidal environments and is considered to be a natural self-cleansing process that enhances recovery rates following a spill (Lee, 2002). In contrast, in lowland rivers with gentle gradients, naturally formed OPAs can lengthen oil spill cleanup times and require deployment of less conventional and more costly sediment remedial measures (Dollhopf and others, 2014; Gouvernement du Quebec, Depot Legal, 2014). For example, in the 2010 Enbridge Line 6B spill of diluted bitumen into the Kalamazoo River, approximately 100 hectares (250 acres) of oiled sediment remaining in impounded sections of the river was removed by dredging and excavation during 2013–14, in response to persistent sheening problems (Dollhopf and Durno, 2011; Dollhopf and others, 2014). Oil globules and OPAs of various sizes, up to a few mm in size, were resuspended during floods, released upon mechanical agitation or physical disturbance of the sediment, and liberated by gas bubbles rising to the surface in a process called ebullition (as happens naturally when methane is produced in freshwater sediments) (fig. 1). Similarly, following the Lac-Mégantic light crude train spill in the Chaudière River, Quebec, Canada, oiled sediments created a challenge to clean-up operations downstream from the spill site over a 30 km reach of the Chaudière River (Gouvernement du Quebec, Depot Legal, 2014).

Modeling the transport and fate of OPAs in riverine systems requires integration of hydrodynamic, sediment transport, and contaminant fate and transport models (Dollhopf and others, 2014; Niu and others, 2010, 2011), while employing some of the same guidelines used for developing conceptual and mathematical models of fate and transport of contaminated sediment at hazardous waste sites (U.S. Environmental Protection Agency, 2005). Simplified fate and transport studies were done for

13

the 2010 Kalamazoo River spill by considering OPAs in a steady state of physical properties, including size, concentration, specific gravity, erosion rates, and settling velocities, as well as hydrocarbon content (Dollhopf and others, 2014). More complex models, accounting for advection/diffusion, settling, resuspension, and breakup characteristics, are being considered for freshwater (riverine and deep-water settings) and marine environments (Lee and others, 2011a; Niu and others, 2011, 2014) and can be built from simpler models that simulate oil slicks (Weaver, 2004).

For the Enbridge Line 6B diluted bitumen spill into the Kalamazoo River, a 2-dimensional (2-D) Environmental Fluid Dynamics Code (EFDC) model was constructed to determine areas of the river prone to resuspension and deposition of submerged oil and oiled sediment under different flow conditions (Hamrick, 1992; Enbridge Energy L.P., 2012a; Dollhopf and others, 2014). Initially, OPAs were assumed to behave similarly to silt-sized particles because the OPAs accumulated in depositional areas and impounded sections of the river with organic- and silt-rich soft sediment. To account for differences in behavior, the model was updated with a new algorithm for OPAs that was incorporated into the sediment transport code of the SNL-EFDC model—a modified version of the original EFDC code developed and maintained by Sandia National Laboratory (James and others, 2005; Thanh and others, 2008). This version of the EFDC model incorporates a custom sediment transport sub-model that is based on the SEDZLJ model algorithms developed by Craig Jones and Wilbert Lick at the University of California – Santa Barbara (Jones and Lick, 2001). The OPA algorithm includes particle classes for representing two types of OPA—a sediment coating on an oil droplet and oil droplets in a particle-dominated aggregate. This algorithm and its application to EFDC and SEDZLJ are under development by the U.S. Army Corps of Engineers Engineering Research and Development Center at the time of this writing (January 2015). Hydrodynamic model results of velocity and horizontal bed shear stress from 2-D and 3-dimensional (3-D) EFDC model simulations of various flows and containment situations on the Kalamazoo River helped to target areas of the 61 km of oil-affected Kalamazoo River where submerged oil and OPAs were subject to resuspension and downriver migration during high flows (Dollhopf and others, 2014; Enbridge Energy L.P., 2012a).

Erosion rates of soft sediment became an important parameter in the modeling because these areas tended to have moderate/heavy oiling, and some of the areas in impoundments switched from depositional to erosional during high flows. The soft sediment was cohesive, and onsite sedflume tests were performed by the U.S. Army Corps of Engineers to parameterize the sediment transport and OPA algorithms in the EFDC models (Perkey and others, 2014). Critical shear stresses of soft sediment with moderate/heavy oiling ranged from 0.1 Pascals (Pa) at the surface to 1.0 Pa at 20 cm beneath the surface (Perkey and others, 2014).

Another approach for fate and transport modeling in rivers is a Lagrangian approach, also known as particle tracking. This approach has been used by the Ven Te Chow Hydrosystems Laboratory at the University of Illinois for the Kalamazoo River and builds on the existing EFDC-based hydrodynamic model.

For impoundments with accumulations of thick fine-grained sediment, the process of bubble formation and release from sediments (ebullition) is likely to be an important mechanism for resuspending OPAs in the water column and releasing oil as sheen on the water surface. Spontaneous releases of oil globules and floating OPAs have been observed regularly in the impounded sections of the Kalamazoo River during 2011–14, resulting in oil sheens at the water surface (Dollhopf and others, 2014). The impoundments had generally 0.5 to 4-m thick accumulations of fine-grained organic-rich sediment which, under anaerobic conditions, allows for bacterial generation of methane (McLinn and Stolzenburg, 2009). These bubbles could rise based on their size and buoyancy, and their release from the sediments could be enhanced by disturbances such as fish and boats movement, falling water levels,

14

and dropping barometric pressures. Methane production and ebullition are enhanced by warm summer water temperatures (as high as 28°C) that promote bacterial activity and reduce the solubility of methane in sediment porewaters.

Ecological Risk and Toxicity of OPAs and Oiled Sediment

The aquatic toxicity of OPAs is of interest, whether the OPAs formed through addition of minerals as a dispersant or from association of oil droplets with suspended inorganic and organic particles naturally present in a water body after the spill. Once oil droplets are aggregated with particles and submerge, associated contaminants, especially polycyclic aromatic hydrocarbons (PAHs), become a potential problem to suspended and benthic aquatic organisms, including plankton, zooplankton, invertebrates, mussels, and clams, and any higher level organisms that consume them (Long and others, 1998; MacDonald and others, 2000; Passow and others, 2012; Almeda and others, 2013). On the other hand, as illustrated during field studies, oil bound up in OPAs may be diluted to below toxicity threshold limits (Lee and others, 2003b) and may become more available for biodegradation (Lee and others, 1997; Lee and Merlin, 1999). An important ecological consideration is closely linked to the turbulent energy of the environment with more risk associated with submerged OPAs in depositional or low energy environments. Freshwater depositional environments are common in low-gradient rivers, river mouths and harbors, impoundments, ponds, lakes, and wetlands. Low-energy marine environments are likely similar (Niu and others, 2011). Thus, a major factor in ecological risk is whether the OPAs are physically diluted in suspension or concentrated in deposition. The added context of water depth and the geographic extent are also important. However, oil droplets and OPAs have a size range similar to that of planktonic food sources for zooplankton, and biogeochemical processing by organisms could increase or decrease toxicity within different components of the aquatic food web (Passow and others, 2012; Almeda and others, 2013).

Data are sparse on the specific toxicity of OPAs in marine and freshwater environments but there are a few studies to draw upon. Qualitative analysis indicated that residual oil was in a highly biodegraded (that is, less toxic) state in suspended particulate material associated with OPA formation from surf washing operations during the Sea Empress Spill in the United Kingdom (Lee and others, 1997). In terms of the application of bioassays, samples recovered from sediment traps deployed in the immediate area off an experimentally oiled beach site in Svalbard, Norway, remediated by the enhancement of OPA formation by surf-washing, were found to be within Environment Canada's acceptable regulatory limits for the disposal of dredge spoils (Lee and others, 2003a; Lee and others, 2003b).

For freshwater riverine environments, limited acute toxicity testing was done for oiled sediment in the Kalamazoo River after the Line 6B oil release (Bejarano and others, 2012). As part of a Net Environmental Benefits Analysis, effects on aquatic organisms from weathered oil were assessed in laboratory acute toxicity studies of seven sediment samples collected from oil-affected backwater habitats along the Kalamazoo River in February 2012, about 19 months post-spill (Bejarano and others, 2012). Ten-day whole sediment toxicity tests using *Chironomus dilutus* (a species of midge) and *Hyalella azteca* (an amphipod crustacean) were performed by the Great Lakes Environmental Center, Inc., and included survival, growth and biomass as the toxicity endpoints (Great Lakes Environmental Center, 2012). Results from the toxicity tests indicated that *Chironomus dilutus* were more sensitive to oiled sediment (and presumably OPAs) than *Hyalella azteca* but that all samples exceeded the minimum survival (70 percent) and growth (0.48 mg ash-free dry weight at test termination) criteria for acceptable controls for the *C. dilutus* tests (Great Lakes Environmental Center, 2012).

15

Chemical analyses (PAHs, total extractable hydrocarbons) and sediment characterization (total organic carbon and sediment composition) were performed on a subset of the above described Kalamazoo River sediment toxicity samples (Bejarano and others, 2012; Great Lakes Environmental Center, 2012). Potential adverse acute and chronic effects on benthic organisms were evaluated using the Equilibrium Sediment Benchmark Toxic Unit Approach (U.S. Environmental Protection Agency, 2003) for sediment PAH data from the same samples used for the bioassays. The results from these analyses indicate that sediment from two heavily oiled sites and one lightly oiled site may pose acute and chronic risks to benthic fauna (*Chironomus dilutus* and *Hyalella azteca*). However, further analyses of the toxicity results in the context of several other sediment characteristics (chemical and physical) showed that unrelated variables, such as percentage of silt in the sediment sample, may have affected survival (table 1). On the basis of the weight of evidence approach and additional risk metrics, it is possible that residual oil from the Enbridge Line 6B oil spill at two heavily and one lightly oiled area may pose some risks to benthic receptors. Chronic toxicity effects from the Enbridge Line 6B residual oil remain unknown at the time of this writing (January 2015).

Table 1. Nonparametric Spearman's Rho correlation coefficients between acute sediment toxicity test results and analytical variables using *Chironomus dilutus* and *Hyalella azteca*. Highlighted cells indicate a statistically significant correlation at α=0.05. Negative correlation coefficients indicate that survival, growth, and biomass were reduced in sediment with higher concentrations of low molecular weight polyaromatic hydrocarbons (PAHs) and total extractable hydrocarbons (TEHs) (from Bejarano and others, 2012).

[LMW, low molecular weight; HMW, high molecular weight; µg/kg, micrograms per kilogram; mg/kg, milligrams per kilogram; TPAH, total polyaromatic hydrocarbons; TOC, total organic carbon; %, percent]

Variables	*Chironomus dilutus*			*Hyalella azteca*		
	Survival	Growth	Biomass	Survival	Growth	Biomass
Sum LMW-PAH (µg/kg)*	-0.53	-0.47	-0.51	-0.44	-0.18	-0.17
Sum HMW-PAH (µg/kg)*	-0.45	-0.36	-0.40	-0.36	-0.20	-0.17
TPAH (µg/kg)	-0.49	-0.43	-0.47	-0.39	-0.22	-0.21
TEH (mg/kg)**	-0.52	-0.53	-0.54	-0.47	-0.29	-0.39
%TOC	-0.67	-0.35	-0.42	0.04	-0.65	-0.65
% Gravel	-0.08	0.02	0.03	0.01	0.07	0.18
% Sand	0.56	0.40	0.41	0.23	0.41	0.54
% Silt	-0.54	-0.52	-0.52	-0.36	-0.44	-0.55
% Clay	-0.53	-0.21	-0.25	-0.13	-0.41	-0.53

*Low molecular weight (LMW) PAHs include Naphthalene to Benzo(b)fluorine (38 analytes), whereas high molecular weight (HMW) PAHs include Fluoranthene to Benzo[g,h,i]perylene (26 analytes).

** Total Extractable Hydrocarbons (C9-C44; TEH).

Summaries of the physical effects from burial of benthic organisms by deposited OPAs can be found in available literature on burial effects from agitation dredging (Chapman, 2012) and on sediment deposition in streams (Waters, 1995). Aquatic organisms most likely affected by burial are fish eggs, larvae, and fry; sessile filter feeders such as mussels; and macrophytes (Chapman, 2012; Morton, 1977; and studies cited in Kaplan and others, 1974; Erftemeijer and Lewis, 2006). For marine benthic organisms, recommendations have been made to limit disposed sediment to 15 cm, but species survival is highly variable, with some species destroyed by as little as 5 cm (OSPAR, 2008) and fish eggs by as little as a few mm (Berry and others 2003; see other citations in Chapman, 2012). Deposition effects vary by species requirements, extent and spatial connection of habitat types, and size of the waterbody.

16

Effects of Ice in Northern Climates on OPA Formation and Spill Response

Most of the cold-condition studies that have been conducted have looked at the behavior of spilled oil and not how the oil interacted with particles to form OPAs (Fingas and Hollebone, 2003; Lee and others, 2011b; Wang and others, 2013) under controlled laboratory and pilot-scale tank studies. Lee and others (2011b) summarize findings from laboratory studies funded by the Canadian Coast Guard to elucidate the potential significance of OPA formation under cold climatic conditions that included ice (Cloutier and others, 2005; Khelifa and others, 2005c). These studies showed that OPAs can form quickly with strong turbulence, within the first 10 minutes of a spill. Within 40 minutes, most of the oil was converted to OPAs. Brackish water (18 ppt) with slush and broken ice had similar results with strong turbulence. Most particles were less than 1 mm in diameter and about 50 percent of the oil was physically dispersed within 30 minutes (Blouin and Lee, 2007; Cloutier and Doyan, 2008).

Field trials in the St. Lawrence River estuary near Matane, Quebec were conducted during the winter to further evaluate the feasibility of enhanced OPA formation as a spill response countermeasure in ice-infested waters (Lee, Li and others, 2011b). An icebreaker's propeller was used to generate strong turbulence during this exercise to facilitate the formation of OPAs with experimentally released fuel oil sprayed with slurry of fine-grained chalk using the fire hose system on board the ship. Visual observations and results of laser particle size analysis (LISST) indicate that fuel oil physically dispersed as OPA into the water column by this experiment did not readily reform a surface slick. Without the addition of mineral fines and consequential OPA formation, the fuel oil resurfaced within minutes and was difficult to recover because of interference by large ice blocks. Half of the total petroleum hydrocarbons in recovered samples biodegraded after 56 days incubation at a temperature of 0.5 °C, which is most likely because of microbes in the water that were well adapted to their surrounding environment, despite the low temperatures.

Although not specific to OPAs, Belore (2010) provided a detailed description of simulations of oil and condensate spills over a range of expected temperatures at the marine trans-shipment terminal and confined channel assessment area (CCAA) of concern for syncrude synthetic light oil, Condensate Blend (CRW), Cold Lake bitumen diluted with condensate, and MacKay River heavy bitumen diluted with Suncor synthetic light oil (MKH). The simulations included a hypothetical marine terminal spill and three hypothetical tanker spills for Emilia Island, Principe Channel, and Wright Sounds for spring, summer, fall, and winter conditions. The tests did not consider interactions between oil and particulate matter, but they provided a thorough set of physical properties and behaviors for these oils including density, viscosity, interfacial tension, pour point, flash point, evaporation, emulsion formation, and oil adhesion.

The formation of OPAs and its effect on promoting dispersion of spilled residual oil may vary because of changes in the properties of the oil, water, particle type, temperature, and extent of ice cover. For example, the viscosity of diluted Cold Lake Blend ranges over an order of magnitude from summer water temperatures (for example, 393.2 square millimeters per second (mm^2/s) at 15 °C) to winter water temperatures (1437.8 mm^2/s at 1 °C) (Belore, 2010).

Biodegradation and toxicity need more research because potential exposure and biological activity are affected by temperature. Recent results by McFarlin and others (2014) found that oil degrading microorganisms were present in surface, middle, and deep water samples from the Arctic Ocean and that oil biodegradation potential exists for offshore Arctic environments; however, this study did not specifically look at biodegradation of OPAs.

Researchers from the Institute of Northern Engineering–University of Alaska Fairbanks and NewFields LLC have conducted several studies of the toxicity of physically and chemically dispersed

oil in arctic environments (McFarlin and others, 2011) that provide some insights into OPA toxicity. In one study, the toxicity of physically versus chemically dispersed oil to selected arctic species representative of the Beaufort and Chukchi Seas was examined at typical arctic water temperatures of 2 °C (McFarlin and others, 2011). Using fresh Alaska North Slope oil, physically dispersed under increased mixing energy in a laboratory, spiked exposure toxicity testing was performed for three arctic species: *Calanus glacialis* (copepod), *Boreogadus saida* (arctic cod), and *Myoxocephalus sp.* (sculpin). When subjected to physically dispersed oil, mean lethal concentration (LC_{50}) values were lower by 3.3 and 3.7 mg/L total petroleum hydrocarbons (TPH) for arctic cod and early season copepods, than the corresponding values in the presence of chemically dispersed oil of 55 mg/L and 22 mg/L, respectively. With the exception of this case, toxicity effects for arctic species from physically dispersed oil were found to be generally no better or worse than for temperate species and warm water temperatures.

In conclusion, the toxicity of suspended and deposited OPAs requires further investigation. OPAs that submerge and accumulate in depositional areas have chemical and physical ecological risks associated with them, either because of toxicity from high concentrations of hydrocarbons, or physical damage, which can result from the smothering and burial of benthic organisms. The appropriate application of laboratory tests to different geographic areas with a range of water depths and water currents needs further consideration.

Operational Considerations

As described in preceding sections, oil can submerge, and OPAs can form rapidly after a spill of light and heavy crude oils, given the right environmental conditions. Key environmental factors that increase the probability of submergence for bitumen spills include (Silliman, 2014):

☐ Low salinity resulting in relatively low water density,

☐ Particles that have relatively high roughness in their surface area or are porous,

☐ High turbidity or high suspended sediment concentrations,

☐ Exposure to sunlight (UV radiation),

☐ Strong currents and mixing energy, and

☐ High temperatures.

Silliman (2014) concludes that if one of these factors is present, then emergency response personnel should equip themselves with response tactics for submerged oil. The following sections describe the state of the science for detection, containment, and recovery of submerged oil, especially submerged OPAs.

Detection

OPAs can be detected by direct observation using specialized microscopy techniques that enable the visualization of oil. On the basis of the strong natural fluorescence of aromatic hydrocarbons and chlorophyll when excited by UV light, Lee and others (1985) devised a bright field transmitted light/UV epi-fluorescence illumination technique that enabled the observation of interaction between chemically dispersed oil droplets and phytoplankton. This technique was subsequently refined and used in a routine manner to characterize and quantify OPAs (Stoffyn-Egli and Lee, 2002; Lee and others, 2003a; Ma and others, 2008). Detailed investigations of the surface and internal structure of OPAs have been conducted by the application of confocal laser scanning microscopy (Stoffyn-Egli and Lee, 2002; Zhang and others, 2010; Wang and others, 2011). Environmental scanning electron microscopy (ESEM) was used to produce high resolution 3-D topographical images of OPA surfaces in their natural state to

18

confirm the existence of "droplet" OPA composed of oil droplets that were stabilized by mineral fines on their surface (Stoffyn-Egli and Lee, 2002). The U.S. Coast Guard's Research and Development Center recently specified requirements for submerged oil detection systems that included 80 percent detection probability, 1-m radius of detection, real-time results, reasonable setup time, accommodation of 1.5-m (5-ft) seas and 0.8 m/s (1.5 knot) currents, and coverage of 1.6 km^2 (1 mi^2) in a 12-hour shift (Hansen, 2014). Established on-site mass spectrometer systems to monitor oil in the water column may not be effective if the oil occurs as OPAs or has already settled out. This was the case in the oil-affected reach of the Kalamazoo River.

Laser fluorometers offer the potential for detection of oil in oil-sediment mixtures and were successful in detecting residual oil in pore water in beach deposits along the coast of Taean, South Korea, following the *Hebei Spirit* oil spill (Kim and others, 2010). In addition, trials with submersible fluorometers with an excitation wavelength of 120-325 nanometers (nm) and emission wavelengths of 410-600 nm met with some success for the Kalamazoo River when the OPAs were in suspension during in situ tests of erosion characteristics of deposited oiled sediment from the 2010 Enbridge Line 6B oil release. A limited number of samples collected at the time the OPAs were in suspension were analyzed at the USGS Wisconsin Water Science Center for both absorbance and fluorescence excitation-emission matrices using an Aqualog instrument (Peter Lenaker, U.S. Geological Survey, written commun., 2013). However, once the OPAs are submerged and mixed with bottom sediment the fluorescent properties of the oil are masked by other particles (Lee and others, 2012). As a result of these short-falls identified with current methodologies for oil spill detection in aquatic environments, Hansen (2014) stressed the importance of simultaneous use of multiple systems.

Detection of OPAs by sonar can be difficult because the detectable sonar signature associated with pure oil is diminished when it is mixed with suspended and bottom sediments. Furthermore, particle size is a factor; oil associated with fine-grained (silt and clay-sized) organic-rich particles is difficult to detect by sonar (Hansen, 2014; authors' experience on the Kalamazoo River cleanup).

A novel sediment poling technique was developed for detecting and assessing the spatial distribution of submerged oil and oiled sediment in the Kalamazoo River; it was adapted from studies of contaminated sediment (David Richardson, Tetra Tech, Inc., oral commun., 2011). This became the primary submerged oil assessment tool used in the Kalamazoo River cleanup (Enbridge Energy, L.P., 2013a; Dollhopf and others, 2014). The sediment was agitated using a graduated aluminum pole with a 20-cm-diameter metal disc on the submerged end. If submerged oil was present in the sediment, the agitation action liberated oil from the sediment, allowing it to float to the water surface. The percent coverage of oil sheen and number of globules at the water's surface within 1 m^2 were observed and categorized as none, light, moderate, or heavy according to the field observation submerged oil flowchart (fig. 8). Thickness of soft sediment in depositional areas could be estimated by quantifying the difference between a 1- and 2-hand push of the graduated pole into the sediment. This procedure was used to map the relative concentration and extent of oiled areas to depositional areas of the river with soft sediment (silt and organic matter) accumulations. From 2010 to 2014, over 20,000 poling points were assessed throughout the affected river system. Global positioning system (GPS) coordinates and field observations were recorded upon poling and managed in a geographic information system, which allowed for detailed mapping of sheening as well as bathymetry, substrate, and flow velocity. Some limitations of the method include the need for water temperatures generally greater than 15°C for consistent categorization, velocities less than about 0.3 m/s (otherwise the sheen and globs are swept too quickly downstream), and water depths of generally less than 3 m. At greater water depths, it is unknown whether the liberated oil can rise the full distance to the water surface, resettles, or is transported downstream.

For the Kalamazoo River spill, multiple rounds of sediment cores were collected, and two types of in situ suspended sediment samplers were deployed for monitoring and assessment (Enbridge Energy, L.P., 2011a). About 25 in situ suspended sediment samplers (Phillips and others, 2000) were placed along the 61-km stretch of the affected river to collect any submerged oil and oiled sediment in suspension in the water column that was being transported over a range of flows including during cleanup activities. In addition, about 70 suspended sediment settling jars, also known as sediment traps (Thomas and others, 2007), were placed in depositional areas of the Kalamazoo River with little to no flow to collect particles that were recently in suspension and settled to the river bottom. These jars were similar to column sampling devices used in lacustrine environments for particulate resuspension and chemical fluxes with ponded water or multiple flow directions, such as wave action and longshore currents (Eadie and others, 1984; Murdoch and MacKnight, 1994).

Initially in the cores, globs of submerged oil from the Kalamazoo River Line 6B spill fluoresced under UV light, making it possible to identify the presence and depth of oil in the cores. In 2012, 2 years after the spill, it became necessary to positively identify that the oil in river sediment originated from the spilled oil and not from a previous spill or other background hydrocarbons (Dollhopf and others, 2014). It was at this time that the oil in the sediment cores was becoming more difficult to visually quantify using UV-fluorescence because of dilution, dispersion, and quenching of oil droplets within the sediment matrix (Lee and others, 2012). It then became necessary to identify a chemical fingerprint of the Line 6B oil using forensic oil chemistry techniques that distinguished a signature of triaromatic stearene biomarkers in Line 6B oil that was unique from other oil contaminants present in Kalamazoo River sediment before the spill (G. Douglas, NewFields, written commun., 2014; Dollhopf and others, 2014). This technique was used to quantify the remaining Line 6B oil concentrations in all three types of sediment samples collected in the Kalamazoo River—sediment cores, in situ suspended sediment samples, and recently deposited samples.

Containment

Conventional containment strategies for floating oil do not address the submergence, potential resuspension, and subsurface transport and redistribution of OPAs. OPAs will easily pass underneath a surface boom. Subsurface booms and silt curtains are more effective. An example of the equipment used to keep submerged oil and oiled sediment from the 2010 Line 6B spill from migrating farther downstream in the Kalamazoo River and into Morrow Lake is shown in figure 9A. The top curtain contains a boom similar to conventional setups to trap floating oil. The bottom curtain is meant to cut off bottom currents and promote deposition. This type of containment curtain is oriented at an angle to river currents to maximize settling of OPAs while limiting the chance for new areas of scour (fig. 9B) (Enbridge Energy, L.P., 2012b, 2013b).
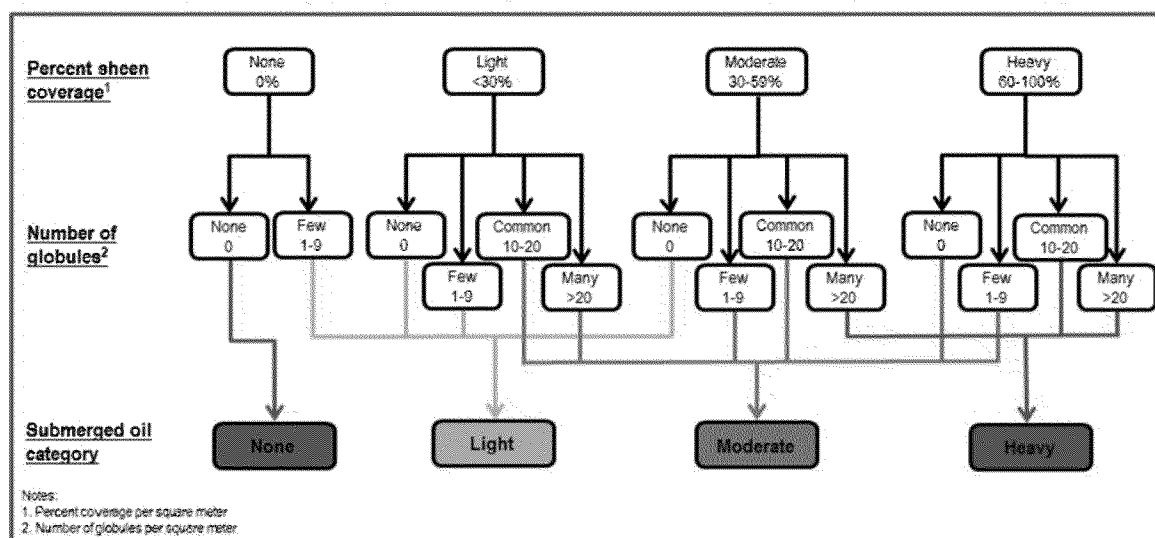
Figure 8. Flowchart used for field observations of submerged oil during poling assessments. (from Enbridge, 2013a; %, percent; <, less than; >, greater than).

Recovery

Recovery techniques for submerged oil and OPAs in freshwater and marine environments are still in the development phase. In a recent document on the fate and transport of potentially spilled oil associated with the proposed Energy East Pipeline Project from Alberta to New Brunswick the following recovery equipment and techniques were recommended by Energy East Pipeline Ltd. (2014): specialized nets, bottom booms, dams and underflow weir dams, dredging, manual recovery, and air injection. Challenges of oil recovery in cold climates, whether in marine or freshwater environments, involve accounting for the following variables: presence of ice, air and water temperatures, remote locations, and low solar radiation (Lee, Li and others, 2011a, b).

Early on in spills, weighted sorbent materials can be dragged along the sea floor or draped along a river bottom to capture submerged oil and OPAs (Hansen, 2014; Enbridge Energy, L.P., 2010). Subsurface sorbent pom-poms (Pister and others, 2009) have been used for oil in suspension. Where oil in deposited OPAs remains at concentrations that cause concerns for benthic organisms or excessive sheening problems, dredging may be necessary (Dollhopf and others, 2014; Gouvernement du Quebec, Depot Legal, 2014).

Enbridge used a combination of agitation toolbox techniques and sheen sweeps in contained areas of the Kalamazoo River, but sheening problems continued in depositional areas after these techniques were used, leading to the adoption of dredging as the final solution (Enbridge Energy, L.P., 2010; Dollhopf and others, 2014). Agitation toolbox techniques used on Kalamazoo River bottom sediment included mechanical agitation through raking, hand-held tillers, and chain drags, along with hydraulic agitation using hand-held water jets arranged as a single wand or on a rotating head (known as stingers) and vessel-mounted or dragged spreader bars with multiple water jets (Enbridge Energy L.P., 2011b). Conventional oil skimming techniques and sheen sweeps were used in response operations in the Kalamazoo River cleanup during periods of spontaneous release of oil globules from depositional areas of the river.

21

A
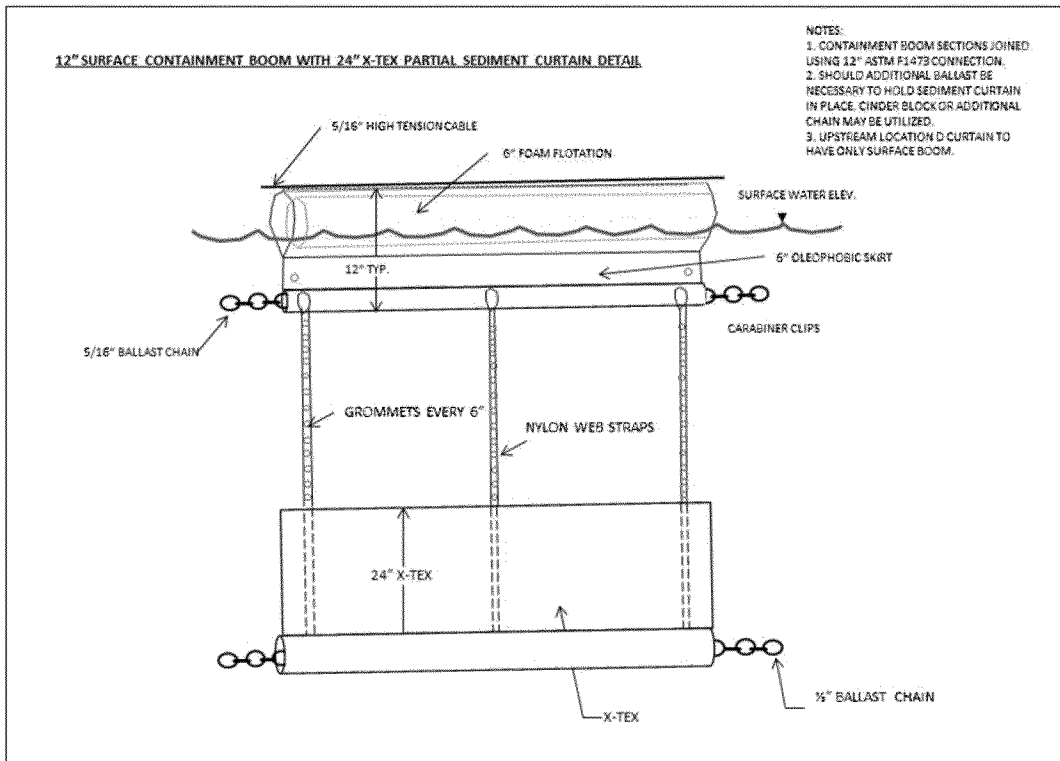
B

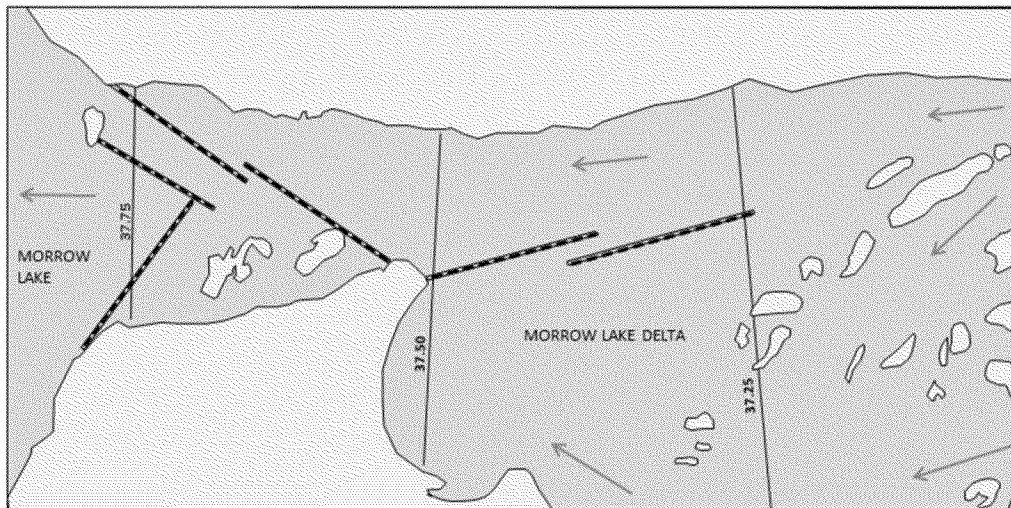Figure 9. A, Diagram of subsurface curtain boom, and B, map of containment boom locations for submerged oil in Morrow Lake Delta from river miles 37.25 to 37.75, Kalamazoo River, Michigan related to the Enbridge Line 6B oil release. Blue arrows on map show general flow direction from right to left. Bold dashed lines are containment boom locations. Redrawn diagrams from Enbridge Energy, L.P. (2013b) containment permits.

22

Some of the methods that have been used for OPAs in suspension and on the bottom along shorelines include (Pister and others, 2009)

☐ Weighted sorbent materials (for example, plastic pom-poms),

☐ Dredging,

☐ Natural attenuation,

☐ Vacuum truck (limited by access),

☐ Small portable submersible pumps,

☐ Debris removal and wrack cleaning,

☐ Sediment reworking,

☐ Flooding, and

☐ Low and high pressure flushing (ambient water) (may leave a significant quantity of oil that requires additional effort).

Techniques that were generally not recommended for marine shorelines and beaches include (Pister and others, 2009)

☐ Offshore barriers and berms,

☐ Mechanical oil removal,

☐ Vegetation removal,

☐ Low and high pressure flushing (hot water),

☐ Steam cleaning,

☐ Sand blasting,

☐ Solidifiers,

☐ Shoreline cleaning agents, and

☐ Natural microbe seeding.

Unfortunately, there is not a simple operational endpoint for spill clean-up operations when it comes to residual OPAs. Remediation for each spill, whether in marine or freshwater environments, can benefit by the development of a Net Environmental Benefit Analysis, which weighs the benefits and drawbacks of leaving oil in place rather than causing further physical damage to aquatic habitats by aggressive removal techniques such as dredging or agitation (Efroymson and others, 2003; Rayburn and others, 2004; Bejarano and others, 2012). It cannot be automatically assumed that in all situations the oil concentrations in deposited OPAs will fall below toxic concentrations during a short period of time as a result of natural attenuation (dilution and biodegradation). Furthermore, it is important to note that the biodegradation of residual oil associated OPA is disadvantaged under anaerobic conditions that form after burial (Lee, 2000). However, depending on the spatial extent of the OPAs, the environmental setting, or presence of sensitive habitat, oil concentrations in OPAs may be adequately diluted to warrant no recovery and allow natural attenuation to happen (Lee and others, 2011a; Bejarano and others, 2012; Fitzpatrick and others, 2013).

Future Science Needs

This report has summarized the state of knowledge regarding the formation of OPAs in natural waters, their eventual transport and fate, and considerations for cleanup of oil spills. The existing knowledge base is insufficient but rapidly growing with recent observations from large spills in freshwater and brackish riverine environments, additional laboratory tests and modeling, and studies of environmental effects of proposed new and expanding pipeline systems in North America carrying bitumen products (http://nas-sites.org/dilbit/). Specific science needs for submerged oil and OPAs are listed below.

- Laboratory experiments of resuspension and breakup of OPAs.
- Updated and new models and simulations of fate and transport of oil and OPAs in freshwater and cold climate environments with a range of oil and sediment types.
- Quantitative monitoring and mapping of large areas of OPAs in water depths greater than 3 m.
- Refinement of the Kalamazoo River poling technique with deployment of a fluorometer in the plume of sediment OPAs resuspended by the poling agitation.
- Monitoring and assessment of transport and fate of spreading oil in ice and below ice.
- Field trials in cold climates. More study is needed using realistic field trials or field observations of OPA formation during oil spills. Especially needed are studies of freshwater environments in and around the Great Lakes coastal environments and river mouths.
- Investigation of potential effects on benthic invertebrate communities from residual oil and OPAs in depositional environments including burial and smothering as well as hydrocarbon toxicity in marine, freshwater, and cold-climate environments.
- Investigation of OPA toxicity and physical effects on habitat. Not enough is known yet about the toxicity of OPAs, especially chronic toxicity and routes of exposure, and application of laboratory results to specific aquatic habitats. Data on the potential negative effects of augmented natural dispersion on burial and smothering of benthic organisms is needed, especially for freshwater environments.
- Vulnerability analyses of critical habitats.
- Incorporation of OPA properties into hydrodynamic and sediment transport models.
- Post-spill monitoring and assessment techniques.
- Operation endpoints—monitoring protocols to determine how much cleanup is enough and the manner in which natural attenuation may ameliorate effects in the future.

Summary and Conclusions

Studies of the formation of oil-particle aggregates (OPAs), and related behavior, fate, and toxicity in a wide variety of environments, including freshwater rivers, are of continued interest to researchers as transportation of light and heavy crude oils continues to increase across North America. This report contains an up-to-date review of the state of the science for OPAs from available literature, in terms of formation and stability, use as a physical dispersant, transport and fate, toxicity, behavior in cold climates, operational considerations, and future science needs. Although much is known about OPAs, there remains a good deal of science to be learned, especially in terms of laboratory experiments,

24

flume studies, toxicity and habitat effects, field exercises, and modeling at a range of spatial and temporal scales.

Questions that were investigated for this report, along with brief answers developed from the available literature are listed here.

☐ What is the effectiveness of adding particles to an oil spill for physical dispersion of oil as a spill countermeasure? The effectiveness varies with oil and particle properties and the salinity of water, but in general the addition of particles will almost always result in some OPA formation. The particles act to stabilize oil droplets and prevent them from re-coalescing at the water surface into an oil slick. Some potentially negative consequences occur when OPAs settle to the bottom possibly causing issues with protracted and increased cleanup costs, and loss of habitat to benthic organisms from smothering and burial. The toxicity of OPAs compared to oil droplets in the water column varies or is not known. Because of these negative effects, prescribed sinking of spilled oil, or the use of sinking agents, is prohibited by U.S. Environmental Protection Agency.

☐ What is the long-term fate and transport of OPAs? Particle interactions tend to stabilize the oil droplets. OPAs can be resuspended when currents or mixing energy increases. OPAs can also be released to the water surface through the process of bubble formation and release from sediments (ebullition) for years following a spill.

☐ What are the ecological implications of OPAs? Ecological implications have to do with whether the OPAs stay in suspension or settle out and the geographic extent and water depth of the aquatic habitat. If OPAs stay in suspension, then microbial degradation would be likely increased. If OPAs settle out, ecological effects would be likely from toxicity and physical smothering.

☐ What are the operational considerations for recovery of OPAs? Containment and recovery of submerged OPAs or OPAs in riverine and marine environments require different techniques than those used for floating oil, and a familiarity with hydraulics of sediment transport is helpful.

☐ Are there special circumstances for OPAs in cold climates? OPAs form readily in cold climates and the addition of particles likely acts as a physical dispersant similar to warm climates. The additional difficulty of using conventional skimming techniques for floating oil where there is broken ice makes physical dispersion a more attractive option. However, habitat loss, burial, smothering, and toxicity effects from submerged OPAs need to be considered, especially for shallow freshwater environments.

References Cited

Almeda, R., Wambaugh, Z., Wang, Z., Hyatt, C., Liu, Z., and Buskey, E.J., 2013, Interactions between zooplankton and crude oil: toxic effects and bioaccumulation of polycyclic aromatic hydrocarbons: PLoS ONE v. 8, no. 6, p. 1–21, accessed January 10, 2015, at http://www.plosone.org/article/fetchObject.action?uri=info%3Adoi%2F10.1371%2Fjournal.pone.0067212&representation=PDF.

American Petroleum Institute, 2011, Crude oil category, category assessment document: American Petroleum Institute Petroleum HPV Testing group, January 14, 2011, 108 p., accessed January 10, 2015, at http://www.epa.gov/oppt/chemrtk/pubs/summaries/crdoilct/c14858ca.pdf.

Andrews, A., 2014, Crude oil properties relevant to rail transport safety: in brief: Congressional Research Service, 7-5700, R43401, February 18, 2014, 10 p., accessed January 10, 2014, at https://www.hsdl.org/?view&did=751042.

Association of American Railroads, 2014, Moving crude oil by rail: Association of American Railroads, September 2014, accessed January 10, 2015, at https://www.aar.org/BackgroundPapers/Crude%20Oil%20by%20Rail.pdf.

Atlas, R.M., and Hazen, T.C., 2011, Oil biodegradation and bioremediation: a tale of the two worst spills in U.S. history: Environmental Science and Technology, v. 45, p. 6,709–6,715.

Attanasi, E.D., and Meyer, R.F., 2007, Natural bitumen and extra-heavy oil, *in* Trinnaman, J., and Clarke, A., eds., 2007 Survey of Energy Resources: World Energy Council, p. 119–143.

Bandara, U.C., Yapa, P.D., and Xie, H., 2011, Fate and transport of oil in sediment laden marine waters. Journal of Hydro-environment Research, v. 5, p. 145–156.

Bejarano, A.C., Michel, J., and Williams, L., 2012, Net Environmental Benefit Analysis (NEBA) relative risk ranking conceptual design, Kalamazoo River system, Enbridge Line 6B Release: Enbridge Line 6B MP 608, Marshall, MI, August 8, 2012; document and appendixes; AR-0963.

Belore, R., 2010, Properties and fate of hydrocarbons associated with hypothetical spills at the marine terminal and in the confined channel assessment area: Ottawa, Ontario, SL Ross Environmental Research Ltd., Technical Data Report, [variously paged].

Berry, W., Rubinstein, N., Melzian, B., and Hill, B., 2003, The biological effects of suspended and bedded sediment (SABS) in aquatic systems, a review: Internal Report. August 20, 2003: U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Laboratory, Narragansett, RI, and Duluth, MN, accessed January 10, 2015, at http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/pollutants/sediment/upload/2004_08 _17_criteria_sediment_appendix1.pdf

Blouin, M., and Lee, K., 2007, Oil mineral aggregate formation in ice-infested waters: Proceedings of the 2007 International Oil & Ice Workshop. Minerals Management Service, Herndon, Va.

Boufadel, M.C., Li, H., Suidan, M.T., and Venosa, A.D.. 2007, Tracer studies in a laboratory beach subjected to waves: Journal of Environmental Engineering v. 133, no. 7, p. 722–732.

Boufadel, M.C., Nasab, A-A., Geng, X., Galt, J., and Torlapati, J., 2014, Simulation of the landfall of the *Deepwater Horizon* oil on the shorelines of the Gulf of Mexico: Environmental Science and Technology, v. 48, p. 9,496−9,505.

Boufadel, M.C., Youness, S., Van Aken, B., Wrenn, B.A., and Lee, K., 2010, Nutrient and oxygen concentrations within the sediments of an Alaskan beach polluted with *Exxon Valdez* Oil Spill: Environmental Science and Technology, v. 44, p. 7,418–7,412.

Bragg, J.R., and Owens, E.H., 1994, Clay–oil flocculation as a natural cleansing process following oil spills—Part 1: Studies of shoreline sediments and residues from past spills: Proceedings of the 17th Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Environment Canada, Ottawa, Ont., p. 1–23.

Bragg, J.R., and Yang, S.H., 1995, Clay-oil flocculation and its role in the natural cleansing in Prince William Sound following the Exxon Valdez oil Spill, *in* Wells, P.G., Butler, J.N., Hughes, J.S., eds., Exxon Valdez oil spill: fate and effects in Alaskan waters: Philadelphia, Pa., ASTM STP 1219, p. 178–214.

26

Center of Offshore Oil and Gas Environmental Research, 2004, The COOGER Update, March 2004, v. 1, no. 1, 6 p., accessed January 10, 2015, at http://www.dfo-mpo.gc.ca/science/coe-cde/cooger-crepge/newsletter/mar04_e.PDF.

Chapman, J., 2012, Review of potential ecological effects of sediment agitation, Appendix B, *in* Bejarano, A.C., Michel, J., and Williams, L., Net Environmental Benefit Analysis (NEBA) relative risk ranking conceptual design, Kalamazoo River system, Enbridge Line 6B Release: August 8, 2012; Unpublished document and appendixes; AR-0963.

Clark, M.M., 2009, Transport modeling for environmental engineers and scientists (2d ed.): Hoboken, New Jersey, John Wiley and Sons, Inc., 664 p.

Cloutier, D., Amos, C.L., Hill, P.R., and Lee, K., 2003, Oil erosion in an annular flume by seawater of varying turbidities: A critical bed shear stress approach: Spill Science and Technology Bulletin, v. 8, p. 83–93.

Cloutier, D., and Doyon, B., 2008, OMA Formation in Ice-Covered Brackish Waters: Large-Scale Experiments, *in* Davidson, W.F., Lee, K., and Cogswell, A., (eds.), Oil Spill Response: A Global Perspective: New York, Springer, p. 71–88.

Cloutier, D., Gharbi, S., and Boule, M., 2005. On the oil-mineral aggregation process: A promising response technology in ice-infested waters: Proceedings of the 2005 International Oil Spill Conference, Miami Beach, FL, USA, p. 527-531.

Coastal Response Research Center, 2007, Submerged oil—state of the practice and research needs: Durham, New Hampshire, Coastal Response Research Center, 29 p. + appendix.

Committee for a Study of Pipeline Transportation of Diluted Bitumen, 2013, Effects of diluted bitumen on crude oil transmission pipelines: Washington, D.C., Transportation Research Board Special Report 311, 132 p.

Crude Quality, Inc., 2014, Crudemonitor.ca., accessed January 10, 2015, at http://www.crudemonitor.ca/home.php.

Delvigne, G.A.L., and Sweeney, C.E., 1988, Natural dispersion of oil: Oil and Chemical Pollution, v. 4, no. 4, p. 281-310.

Doelling, P., Davis, A., Jellison, K., and Miles, S., 2014, Bakken crude oil spill, Barge E2MS 303, Lower Mississippi River, February 2014, National Oceanic and Atmospheric Administration, overview presentation, accessed January 10, 2015, at http://www.nrt.org/production/NRT/RRT3.nsf/Resources/May2014_pdf/$File/Bakken_Crude_Spill_E2MS303_Revised.pdf.

Dollhopf, R.H., and Durno, M., 2011, Kalamazoo River Enbridge Pipeline Spill: Proceedings 2011 International Oil Spill Conference, accessed January 10, 2015, at http://ioscproceedings.org/doi/pdf/10.7901/2169-3358-2011-1-422.

Dollhopf, R.H., Fitzpatrick, F.A., Kimble, J.W., Capone, D.M., Graan, T.P., Zelt, R.B., Johnson, R., 2014, Response to heavy, non-floating oil spilled in a Great Lakes river environment: a multiple-lines-of-evidence approach for submerged oil assessment and recovery: Proceedings, 2014 International Oil Spill Conference, Savannah, GA, May 7-9, 2014, p. 434–448, accessed January 10, 2015, at http://ioscproceedings.org/doi/pdf/10.7901/2169-3358-2014.1.434.

Eadie, B.J., Chambers, R.L., Gardner, W.S., and Bell, G.L., 1984, Sediment trap studies in Lake Michigan: Resuspension and chemical fluxes in the southern basin: Journal of Great Lakes Research,

v. 10, p. 307–321, accessed January 10, 2015, at http://www.glerl.noaa.gov/pubs/fulltext/1984/19840004.pdf.

Efroymson, R.A., Nicolette, J.P., Suter, II, G.W., 2003, A framework for Net Environmental Benefit Analysis for remediation or restoration of petroleum-contaminated sites: Oak Ridge National Laboratory ORNL/TM-2003/17.

Enbridge Energy, L.P., 2010, Work plan for permanent recovery of submerged oil and oil-contaminated sediments at priority locations and Ceresco Dam dredging: Enbridge Line 6B MP 608, Enbridge Energy, L.P., Marshall, Mi., 21 p. (Submitted October 7, 2010).

Enbridge Energy, L.P., 2011a, Addendum to the response plan for downstream impacted areas, August 2, 2010 (Revised August 17, 2010 per U.S. Environmental Protection Agency August 17, 2010 letter), Supplement to source area response plan, and supplement to response plan for downstream impacted areas, referred to as operations and maintenance work plan: Enbridge Line 6B MP 608, Enbridge Energy, L.P., Marshall, Mich., 376 p. (Submitted December 4, 2011).

Enbridge Energy, L.P., 2011b, Submerged oil recovery standard operating procedure: Enbridge Line 6B MP 608, Enbridge Energy, L.P., Marshall, Mich., Prepared for Michigan Department of Environmental Quality, June 28, 2011.

Enbridge Energy, L.P., 2012a, Kalamazoo River hydrodynamic and sediment transport model: Enbridge Line 6B MP 608, Marshall, Mich., 70 p., attachments. (Submitted April 20, 2012)

Enbridge Energy, L.P., 2012b, 2012 Morrow Lake Delta and Morrow Lake monitoring and management work plan, Enbridge Line 6B MP 608, Marshall, Mich., November 15, 2012. AR-1720.

Enbridge Energy, L.P., 2013a, Sediment poling standard operating procedure: Enbridge Line 6B MP 608, Marshall, Mich., 11 p. (Submitted May 22, 2013).

Enbridge Energy, L.P., 2013b, Michigan Department of Environmental Quality Permit 13-39-0012-P, April 30, 2013.

Enbridge Energy Partners, L.P., 2013, 2013 crude characteristics, Enbridge Pipelines, Inc., No. 44, accessed January 10, 2015, at http://www.enbridge.com/DeliveringEnergy/Shippers/CrudeOilCharacteristics.aspx.

Energy East Pipeline, Ltd., 2014, Oil fate and transport effects, volume 6: Accidents and malfunctions, Section 3: Crude oil characteristics, environmental fate, transport, and effects: Energy East Pipeline Project, 48 p., accessed March 23, 2015 at https://docs.neb-one.gc.ca/ll-eng/llisapi.dll/fetch/2000/90464/90552/2432218/2540913/2543426/2543068/ESA_V6_S3_OilFateTranspEffects_-_A4E1F4.pdf?nodeid=2543560&vernum=-2.

Environment Canada, 2013, Considerations, Volume 2, Report of the Joint Review Panel for the Enbridge Northern Gateway Project, National Energy Board, Calgary, Alberta, 425 p., accessed January 10, 2015, at http://gatewaypanel.review-examen.gc.ca/clf-nsi/dcmnt/rcmndtnsrprt/rcmndtnsrprtvlm2-eng.pdf.

Erftemeijer, P.L.A., and Lewis, R.R.R. III, 2006, Environmental impacts of dredging on seagrasses: A review: Marine Pollution Bulletin, v. 52, p. 1553–1572.

Fitzpatrick, F.A., Graan, T., Aboulafia, I., Capone, D., Bejarano, A., DeLong, M., Hamilton, S., Michel, J., and Williams, L., 2013, Application and Integration of Net Environmental Benefit Analysis (NEBA) with Tactical Areas: Ceresco Impoundment, Mill Ponds, and Morrow Lake Delta, December 2012 Update in Support of the Kalamazoo River NEBA: Marshall, MI, AR-1710.

28

Fingas, M.F., and Hollebone, B.P., 2003, Review of behavior of oil in freezing environments: Marine Pollution Bulletin v. 47, p. 333–340.

Frittelli, J., Andrews, A., Parfomak, P.W., Pirog, R., Ramseur, J.L., Ratner, M., 2014, U.S. rail transportation of crude oil: background and issues for Congress: Congressional Research Service, December 4, 2014, accessed January 10, 2015, at http://fas.org/sgp/crs/misc/R43390.pdf.

Geng, X., Boufadel, M.C., and Wrenn, B., 2013, Mathematical modeling of the biodegradation of residual hydrocarbon in a variably-saturated sand column: Biodegradation, v. 24, no. 2, p. 153–163.

Gong, Y., Zhao, X., Cai, Z., O'Reilly, S.E., Hao, X., and Zhao, D., 2013, A review of oil, dispersed oil and sediment interactions in the aquatic environment: influence on the fate, transport, and remediation of oil spills: Marine Pollution Bulletin, v. 79, no. 1–2, p. 16–33.

Gouvernement du Quebec, Depot Legal, 2014, Tragedie ferroviaire de Lac-Mégantic, Rapport du comite expert sur la contamination residuelle, de la riviere Chaudière par les hydrocarbures petroliers: Gouvernement du Quebec, Quebec, 62 p. ISBN: 978-2-550-70519-2.

Grant, A.C., Levy, E.M., Lee, K., and Moffatt, J.D., 1986, PISCES IV research submersible finds oil on Baffin shelf: Current Research, Part A, Part A: Geological Survey Canada, 86-1A, p. 65–69.

Great Lakes Environmental Center, Inc., 2012, Preliminary 10-day whole sediment toxicity test report *Hyalella azteca* and *Chironomus dilutus* Kalamazoo River sediment sampling, February 2012 Line 6B Spill, Marshall, Michigan: Traverse City, Mich., Great Lakes Environmental Center, March 21, 2012, 8 p. + appendixes.

Hamrick, J. M., 1992, A three-dimensional environmental fluid dynamics computer code: theoretical and computational aspects: Gloucester Point, Va., Virginia institute of Marine Science, Applied Marine Science and Ocean Engineering, Special Report No. 317, p. 1–64.

Hansen, K.A., 2014, Submerged oil response: Proceedings of the Marine Safety & Security Council, U.S. Coast Guard Journal of Safety & Security at Sea, Winter 2013–2014, p. 22–25.

Hoard, C.J., Fowler, K.K., Kim, M.H., Menke, C.D., Morlock, S.E., Peppler, M.C., Rachol, C.M., and Whitehead, M.T., 2010, Flood-inundation maps for a 15-mile reach of the Kalamazoo River from Marshall to Battle Creek, Michigan, 2010: U.S. Geological Survey Scientific Investigations Map 3135, 6 page pamphlet, 6 sheets, scale 1:100,000.

James, S.C., Jones, C., and Roberts, J.D., 2005, Consequence management, recovery & restoration after a contamination event: Sandia National Laboratory Report SAND2005-6797.

Jones, C., and Lick, W., 2001, SEDZLJ, A sediment transport model: Final Report, Santa Barbara, Calif.: Department of Mechanical and Environmental Engineering, University of California, May 29, 2001.

Kaku, V.J., Boufadel, M.C., Venosa, A.D., 2006, Evaluation of mixing energy in laboratory flasks used for dispersant effectiveness testing: Journal of Environmental Engineering, v. 132, no. 1, p. 93–101.

Kaplan, E.H., Welker, J.R., and Kraus, M.G., 1974, Some effects of dredging on populations of macrobenthic organisms: Fishery Bulletin, v. 72, no. 2, p. 445–480.

Khelifa, A., Stoffyn-Egli, P., Hill, P.S., Lee, K., 2002, Characteristics of oil droplets stabilized by mineral particles: effect of oil types and temperature: Spill Science and Technology Bulletin, v. 8, no. 1, p. 19–30.

Khelifa, A., Hill, P.S., Lee, K, 2005a, The role of oil-sediment aggregation in dispersion and biodegradation of spilled oil, *in* Al-Azab, M., El-Shorbagy, W., and Al-Ghais, S., eds., Oil Pollution and its Environmental Impact in the Arabian Gulf Region: Chapter 10, p. 131–145.

29

Khelifa, A., Hill, P.S., Lee, K., 2005b, A comprehensive numerical approach to predict oil-mineral aggregate (OMA) formation following oil spills in aquatic environments: Proceedings International Oil Spill Conference, May 2005, http://ioscproceedings.org/doi/abs/10.7901/2169-3358-2005-1-873.

Khelifa, A., Ajijolaiya, L.O., MacPherson, P., Lee, K., Hill, P.S., Gharbi, S., and Blouin, M., 2005c, Validation of OMA formation in cold brackish and sea waters: Proceedings of the 28th Arctic and Marine Oilspill Program (AMOP) Technical Seminar on Environmental Contamination and Response, Environment Canada, Ottawa, Ontario, p. 527–538.

Kim, M., Yim, U.H., Hong, S.H., Jung, J.H., Choi, H.W., An, J., Won, J., and Shim, W.J., 2010, *Hebei Spirit* oil spill monitored on site by fluorometric detection of residual oil in coastal waters off Taean, Korea: Marine Pollution Bulletin, v. 60, no. 3, p. 383–389.

King, T.L., Robinson, B., Boufadel, M., and Lee, K., 2014, Flume tank studies to elucidate the fate and behavior of diluted bitumen spilled at sea: Marine Pollution Bulletin, v. 83, p. 32–37.

King, T., Robinson, B., C. McIntyre, S. Ryan, P. Toole, F. Saleh, M. C. Boufadel, and K. Lee, 2015, Fate of surface spills of Cold Lake Blend diluted bitumen treated with dispersant and minerals fines in a wave tank: Environmental Engineering Science.

Lee, K., 2000, In situ bioremediation of oiled shoreline environments: Opportunities for Advancement of Environmental Applications of Marine Biotechnology, Proceedings of the October 5-6, 1999, National Research Council of the National Academy of Sciences and the National Academy of Engineering, Washington, DC., National Academy Press, p. 44–60.

Lee, K., 2002, Oil-particle interactions in aquatic environments: influence on the transport, fate, effect, and remediation of oil spills: Spill Science and Technology Bulletin, v. 8, no. 1, p. 3–8.

Lee, K., Boudreau, M., Bugden, J., Burridge, L., Cobanli, S.E., Courtenay, S., Grenon, S., Hollebone, B., Kepkay, P. Li, Z., Lyons, M. Niu, H. King, T.L., MacDonald, S., McIntyre, E.C., Robinson, B., Ryan S.A., and Wohlgeschaffen, G., 2011, State of knowledge review of fate and effect of oil in the arctic marine environment: Report for the National Energy Board of Canada, Arctic Roundtable: State-of-knowledge review of fate and effects of oil in arctic offshore: Fisheries and Oceans Canada, 259 p., accessed on January 14, 2015, at https://docs.neb-one.gc.ca/ll-eng/llisapi.dll/fetch/2000/90463/621169/700096/704342/A2A8R2_-_NEB_State_of_Knowledge_Review_of_Fate_and_Effect_of_Oil_DFO_COOGER.pdf?nodeid=704343&vernum=0.

Lee, K., Bugden, J., Cobanli, S., King, T., McIntyre, C., Robinson, B., Ryan, S., and Wohlgeschaffen, G., 2012, UV-epifluorescence microscopy analysis of sediments recovered from the Kalamazoo River: Dartmouth, Nova Scotia, Centre for Offshore Oil, Gas and Energy Research (COOGER) Report, October 24, 2012.

Lee, K., and Jarvis, R., 2004, Scientific journal dedicates issue to COOGER research: The COOGER update, March 2004, v. 1, no. 1, p. 3.

Lee, K., Li, Z., Kepkay, P., Boufadel, M.C., and Venosa, A.D., 2008, Effects of chemical dispersants on oil-mineral-aggregation in a wave tank: Proceedings of the 2008 International Oil Spill Conference, Savannah, Georgia, p. 633–638.

Lee, K., Li, Z., Niu, H., Kepkay, P., Zheng, Y., Boufadel, M., and Chen, Z., 2009, Enhancement of oil-mineral-aggregate formation to mitigate oil spills in offshore oil and gas activities: Final Report (Contract No. M07PC13035) submitted to Minerals Management Service, March 30, 2009, 91 p.

Lee, K., Li, Z., Robinson, B., Kepkay, P.E., Blouin, M., and Doyon, B., 2011b, Oil spill countermeasures in the Arctic: Proceedings of the International Conference on Oil Spill Risk

Management: Preparedness, Response and Contingency Planning in the Shipping and Offshore Industries, 7–9 March, Malmo Borshus, Sweden, Bellefontaine, Neil, and Linden, Olof, eds., WMU Publications, p. 93–108.

Lee, K, Li, Z., Robinson, B., Kepkay, P.E., Blouin, M., and Doyon, B., 2011b, Field trials of *in-situ* oil spill countermeasures in ice-infested waters: Proceedings of the International Oil Spill Conference, p. 1-16, accessed on January 14, 2015, at http://ioscproceedings.org/doi/pdf/10.7901/2169-3358-2011-1-160.

Lee, K., Lunel, T., Wood, P., Swannell, R., and Stoffyn-Egli, P., 1997, Shoreline clean up by acceleration of clay-oil flocculation processes: Proceedings of the 1997 International Oil Spill Conference (Prevention, Behavior, Control and Cleanup), Fort Lauderdale, Florida, p. 235–240.

Lee, K., and Merlin, F.X., 1999, Bioremediation of oil on shoreline environments: development of techniques and guidelines: Pure Applied Chemistry, v. 71, no. 1, p. 161–171.

Lee, K., and Stoffyn-Egli, P., 2001, Characterization of oil-mineral aggregates: Proceedings of the 2001 International Oil Spill Conference, Tampa Florida, p. 991–996.

Lee, K., Stoffyn-Egli, P., and Owens, E. H., 2002, The OSSA II pipeline oil spill: Natural mitigation of a riverine oil spill by oil-mineral aggregate formation: Spill Science & Technology Bulletin, v. 7, p. 149–154.

Lee, K., Stoffyn-Egli, P., and Owens, E.H., 2001, Natural dispersion of oil in a freshwater ecosystem: Desaguadero pipeline spill, Bolivia: Proceedings of the 2001 International Oil Spill Conference, Tampa Florida, p. 1445–1448.

Lee, K., Stoffyn-Egli, P., Tremblay, G.H., Owens, E.H., Sergy, G.A., Guénette, C.C., and Prince, R.C., 2003a, Oil-mineral aggregate formation on oiled beaches: Natural attenuation and sediment relocation: Spill Science and Technology Bulletin, v. 8, p. 285–296.

Lee, K., Stoffyn-Egli, P., Wood, P.A., Lunel, T., 1998, Formation and structure of oil-mineral fines aggregates in coastal environments: Proceedings of the 21st Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Environment Canada, Ottawa, Ontario, p. 911–921.

Lee, K., Weise, A.M., and St-Pierre, S., 1996, Enhanced oil biodegradation with mineral fine interaction: Spill Science and Technology Bulletin, v. 3, no. 4, p. 263–267.

Lee, K., Wohlgeschaffen, G., Tremblay, G.H., Johnson, B.T., Sergy, G.A., Prince, R.C., Guénette, C.C., and Owens, E.H., 2003b, Toxicity evaluation with the Microtox test to assess the impact of in-situ oiled shoreline treatment options: Natural attenuation and sediment relocation: Spill Science and Technology Bulletin, v. 8, p. 273–284.

Lee, K., Wong, C.S., Cretney, W.J., Whitney, F.A., Parsons, T.R., Lalli, C.M., and Wu, J., 1985, Microbial response to crude oil and Corexit 9527: SEAFLUXES enclosure study: Microbial Ecology, v. 11, p. 337–351.

Li, Z., Kepkay, P., Lee, K., King, T., Boufadel, M., and Venosa, A., 2007, Effects of chemical dispersants and mineral fines on crude oil dispersion in a wave tank under breaking waves: Marine Pollution Bulletin, v. 54, no. 7, p. 983–993.

Long, E.R., Field, L.J., and MacDonald D.D., 1998, Predicting toxicity in marine sediments with numerical sediment quality guidelines: Environmental Toxicology and Chemistry, v. 17, p. 714–727.

Ma, X., Cogswell, A., Li, Z., Lee, K., 2008, Particle size analysis of dispersed oil and oil-mineral aggregates with an automated epifluorescence microscopy system: Environmental Technology, v. 29, no. 7, p. 739–748.

31

MacDonald, D.D., Ingersoll, C.G., and Berger, T.A., 2000, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems: Archives of Environmental Contamination and Toxicology, v. 39, p. 20–31.

McFarlin, K.M., Perkins, R.A., Gardiner, W.W., Word, J.D., and Word, J.Q., 2011, Toxicity of physically and chemically dispersed oil to selected arctic species: Proceedings of the 2011 International Oil Spill Conference, Portland, OR, 7 p.

McFarlin, K.M., Leigh, M.B., and Perkins, R.A., 2014, Biodegradation of oil and dispersed oil by Arctic marine microorganisms: Proceedings of the 2014 International Oil Spill Conference, Savannah, GA., Poster.

McLinn, E.L., and Stolzenburg, T.R., 2009, Ebullition-facilitated transport of manufactured gas plant tar from contaminated sediment: Environmental Toxicology and Chemistry, v. 23, no. 11, p. 2298–2306.

Morton, J.W., 1977, Ecological effects of dredging and dredge spoil disposal: A literature review: U.S. Fish and Wildlife Service, Technical Papers of the U.S. Fish and Wildlife Service 94, 33 p.

Murdoch, A., and MacKnight, S.D., 1994, Handbook of techniques for aquatic sediments sampling (2d. ed.): Boca Raton, Fla., CRC Press, 256 p.

Muschenheim, D.K., and Lee, K., 2002, Removal of oil from the sea surface through particulate interactions: review and prospectus: Spill Science and Technology Bulletin, v. 8, p. 9–18.

National Research Council, National Academy of Sciences, 1999, Spills of nonfloating oils: Risk and response: Washington, D.C., National Academy of Science, National Research Council, 87 p.

National Research Council, National Academy of Sciences, 2005, Oil spill dispersants, efficacy and effects: Washington, D.C., National Academies Press, 396 p.

National Research Council, National Academy of Sciences, 2013, An ecosystem services approach to assessing the impacts of the Deepwater Horizon oil spill in the Gulf of Mexico: Washington, D.C., National Academy of Science, National Research Council, 350 p.

Niu, H., Lee, K., Boufadel, M.C., Zhao, L., and Robinson, B., 2014, In situ oil spill countermeasures in ice-infested waters: A modeling study of the fate/behaviors of spilled oil: Proceedings 2014 International Oil Spill Conference, Savannah, GA., p. 1215–1226.

Niu, H., Li, Z., Lee, K., Kepkay, P., and Mullin, J.V., 2011, Modelling the transport of oil-mineral-aggregates (OMAs) in the marine environment and assessment of their potential risks: Environmental Modeling and Assessment, v. 16, p. 61–75.

Niu, H., Li, Z., Lee, K., Kepkay, P., and Mullin, J.M., 2010, A method for assessing environmental risks of oil-mineral-aggregates to benthic organisms: Human and Ecological Risk Assessment, v. 16, no. 4, p. 762–782.

Omotoso, O.E., Munoz, V.A., and Mikula, R.J., 2002, Mechanisms of crude oil–mineral interactions: Spill Science and Technology Bulletin, v. 8, no. 1, p. 45–54.

OSPAR, 2008, Literature review on the impacts of dredged sediment disposal at sea: OSPAR Commission, Biodiversity Series, accessed January 15, 2015, at http://www.ospar.org.

Owens, E.H., and Lee, K., 2003, Interaction of oil and mineral fines on shorelines: review and assessment: Marine Pollution Bulletin, v. 47, p. 397–405.

Passow, U., Ziervogel, K., Asper, V., and Diercks, A., 2012, Marine snow formation in the aftermath of the Deepwater Horizon oil spill in the Gulf of Mexico: Environmental Research Letters, v. 7, p. 1–11.

32

Payne, J.R., Clayton J.R., Jr., Kirstein, B.E., 2003. Oil/suspended particulate material interactions and sedimentation Spill Science Technology Bulletin, v. 8, p. 201–221.

Perez, S., Furlan, P., Hussein, N., Shinn, D., and Crook, R., 2014, Interaction between oil and suspended sediments in class 1-2 rivers: Proceedings, International Oil Spill Conference, Savannah, GA, May 2014, v. 2014, no. 1, p. 299120.

Perkey, D.W., Smith, S.J., and Kirklin, T., 2014, Cohesive sediment erosion field study: Kalamazoo River, Kalamazoo, Michigan: Vicksburg, Miss., U.S. Army Corps of Engineers Research and Development Center, Coastal and Hydraulics Laboratory, Letter Report, 16 p. + appendixes.

Phillips, J.M., Russell, M.A., and Walling, D.E., 2000, Time-integrated sampling of fluvial suspended sediment: A simple methodology for small catchments: Hydrological Processes, v. 14, p. 2589–2602.

Pister, B., Lewis, R.D., and Wiese, K., 2009, Site specific geographic response plan: Cabrillo National Monument, Point Loma, California: Cabrillo National Monument Report, 27 p.

Prince, M.J., and Blanch, H.W., 1990, Bubble coalescence and break-up in air-sparged bubble columns: American Institute of Chemical Engineers Journal, v. 36, no. 10, p. 1485–1499.

Rayburn, T., Whelan, A., Jaster, M., Wingrove, R., 2004, Net Environmental Benefit Analysis for Isle Royale National Park, Final Report: Proceedings from the workshop held January 6-8, 2004, Duluth, MN.

Reddy, C.M., Arey, J.S., Seewald, J.S., Sylva, S.P., Lemkau, K.L., Nelson, R.K., Carmichael, C.A., McIntyre, C.P., Fenwick, J., Ventura, G.T., Van Mooy, B.A.S., and Camilli, R., 2012, Composition and fate of gas and oil released to the water column during the *Deepwater Horizon* oil spill: Proceedings of the National Academy of Sciences of the United States of America, v. 109, no. 50.

Rymell, M., 2009, RP595, Sunken and submerged oils—behavior and response, A report for the Maritime and Coastguard Agency: BMT Cordah Limited, February, 2009.

Sia Partners Energy Outlook, 2011, Oil sands: the oil of the post-oil?: Sia Partners Energy Outlook Weblog, 8-24-2010, accessed January 15, 2015, at http://energy.sia-partners.com/20100824/oil-sands-the-post-oil-oil/.

Silliman, B., 2014, Guidelines to prepare for oil sands product spills in varied aquatic environments: Proceedings, 2014 International Oil Spill Conference, Savannah, GA, May 7–9, 2014, p. 426–433.

Sterling, M.C., Jr., Bonner, J.S., Ernest, A.N.S., Page, C.A., and Autenrieth, R.L., 2005, Application of fractal flocculation and vertical transport model to aquatic sol–sediment systems: Water Resources, v. 39, p. 1818–1830.

Stoffyn-Egli, P., and Lee, K., 2002, Characterization of oil-mineral aggregates: Spill Science and Technology Bulletin, v.8, no. 1, p. 31–44.

Sun, J., and Zheng, X.L., 2009, A review of oil-suspended particulate matter aggregation natural process of cleansing spilled oil in the aquatic environment: Journal of Environmental Monitoring, v. 11, p. 1801–1809.

Thanh, P.H.X., Grace, M.D., and James, S.C., 2008, Sandia National Laboratories Environmental Fluid Dynamics Code: Sediment Transport User Manual: Sandia National Laboratory Report SAND2008-5621.

Thomas, J.D., Lutz, M.A., Bruce, J.L., Graczyk, D.J., Richards, K.D., Krabbenhoft, D.P., Westenbroek, S.M., Scudder, B.C., Sullivan, D.J., and Bell, A.H., 2007, Water-quality characteristics for selected sites within the Milwaukee Metropolitan Sewerage District Planning Area, Wisconsin, February 2004-September 2005: U.S. Geological Survey Scientific Investigations Report 2007–5084, 187 p.

Tsouris, C., and Tavlarides, L., 1994, Breakage and coalescence models for drops in turbulent dispersions: American Institute of Chemical Engineers Journal, v. 40, no. 3, p. 395–406.

U.S. Environmental Protection Agency, 1993, Use of chemical dispersants for marine oil spills: Edison, New Jersey, U.S. Environmental Protection Agency Office of Research and Development, EPA/600/R-93/195.

U.S. Environmental Protection Agency, 2003, Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH Mixtures: Washington, D.C., U.S. Environmental Protection Agency Office of Research and Development, EPA-600- R-02-013.

U.S. Environmental Protection Agency, 2005, Contaminated sediment remediation guidance for hazardous waste sites: U.S. Environmental Protection Agency Office of Solid Waste and Emergency Response, EPA-540-R-05-012 [variable paginated].

U.S. Environmental Protection Agency, 2011, Cleanup continues; focus on submerged oil: U.S. Environmental Protection Agency Fact Sheet, July 2010 Enbridge Oil Spill, August 2011, 2 p., accessed January 15, 2015, at http://www.epa.gov/enbridgespill/pdfs/enbridge_fs_20110811.pdf.

Venosa, A.D., Anasta, P.T., Barron, M.G., Conmy, R.N., Greenberg, M.S., and Wilson, G.J., 2014, Science-based decision making on the use of dispersants in the Deepwater Horizon oil spill, Chapter 1, in Somasundaran, P., Patra, P., Farinato, R.S., Papadopoulos, K., eds., Oil spill remediation: Colloid chemistry-based principles and solutions, (1st ed.): New York, John Wiley and Sons, Inc., p. 1–17.

Wang, C., and Calabrese, R.V., 1986, Drop breakup in turbulent stirred-tank contactors, Part II: Relative influence of viscosity and interfacial tension: American Institute of Chemical Engineers Journal, v. 32, no. 4, p. 667–676.

Wang, W., Zheng, Y., and Lee, K., 2013, Chemical dispersion of oil with mineral fines in a low temperature environment: Marine Pollution Bulletin, v. 72, p. 205–212.

Wang, W., Zheng, Y., Li, Z., and Lee, K., 2011, PIV investigation of oil–mineral interaction for an oil spill application: Chemical Engineering Journal, v. 170, p. 241–249.

Waters, T.F., 1995, Sediment in streams: sources, biological effects, and control: Bethesda, Maryland, American Fisheries Society Monograph 7, 251 p.

Weaver, J.W., 2004, Characteristics of spilled oils, fuels, and petroleum products, 3a, Simulation of oil spills and dispersants under conditions of uncertainty: Washington, D.C., U.S. Environmental Protection Agency, EPA 600/R-04/120.

Weise, A.M., Nalewajko, C., and Lee, K., 1999, Oil-mineral fine interactions facilitate oil biodegradation in seawater: Environmental Technology, v. 20, p. 811–824.

Wood, P., Lunel, T., Bailey, N., Lee, K., and Stoffyn-Egli, P., 1997, Clay-oil flocculation during surf washing at the Sea Empress incident: Proceedings of the 20th Arctic and Marine Oil Spill Program Technical Seminar, p. 1,085–1,105.

Zhang, H., Khatibi, M., Zheng, Y., Lee, K., Zhengkai, L., Mullin, J., 2010, Investigation of OMA formation and the effect of minerals: Marine Pollution Bulletin, v. 60, p. 1433–1441.

Zhao, L., Torlapati, J., Boufadel, M., King, T., Robinson, B., and Lee, K., 2014a, VDROP: a numerical model for the simulation of droplet formation from oils of various viscosities: Chemical Engineering Journal, v. 253, p. 93–106.

Zhao, L., Torlapati, J., King, B. Davidson, T., Boufadel, M., and Lee, K., 2014b, A numerical model to simulate the droplet formation process resulting from the release of diluted bitumen products in marine environment: Proceedings, 2014 International Oil Spill Conference, Savannah, GA, p. 449–462.

USGS

Fitzpatrick and others—Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments—Review of the Science and Future Science Needs—Open-File Report 2015–1076

To: Zhang, Yu (zhang4y5)[zhang4y5@mail.uc.edu]; Sundaravadivelu, Devi[sundaravadivelu.devi@epa.gov]; Zhuang, Mobing (zhuangmg)[zhuangmg@mail.uc.edu]; Elk, Michael[Elk.Michael@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]; Venkatapathy, Raghuraman[Venkatapathy.Raghuraman@epa.gov]; p.campo-moreno@cranfield.ac.uk[p.campo-moreno@cranfield.ac.uk]; Holder, Edith[holder.edith@epa.gov]
From: SantoDomingo, Jorge
Sent: Mon 4/25/2016 8:54:28 PM
Subject: Re: Oil Degradation Data- Dispersant project
ANS_Microcsom_Draft_4_25_16 final Stics .docx

Attached is the latest draft. For those that are co-authors, please read and provide comments ASAP. I included a few others as they might be interested as well. Mobing, I need to discuss with you if there is other data on the different aliphatic and aromatic fractions that could be in this paper, which I know will depend if you are using it in another paper. Pablo, let us know as well on the latter point.

I look forward to reading your comments. From our end I think we are close.

Cheers, jorge

From: Zhang, Yu (zhang4y5) <zhang4y5@mail.uc.edu>
Sent: Monday, April 11, 2016 3:38:18 PM
To: Sundaravadivelu, Devi; Zhuang, Mobing (zhuangmg); SantoDomingo, Jorge; Elk, Michael
Cc: Conmy, Robyn; Venkatapathy, Raghuraman; p.campo-moreno@cranfield.ac.uk; Holder, Edith
Subject: Re: Oil Degradation Data- Dispersant project

Dear All,

Please find the DOSS and oil degradation results for Finasol + ANS experiment in the email. If there's any problem, please let me know.

Regards,

Yu

From: Sundaravadivelu, Devi <sundaravadivelu.devi@epa.gov>
Sent: Thursday, April 7, 2016 3:24 PM
To: Zhuang, Mobing (zhuangmg); Zhang, Yu (zhang4y5); SantoDomingo, Jorge; Elk, Michael
Cc: Conmy, Robyn; Venkatapathy, Raghuraman; p.campo-moreno@cranfield.ac.uk; Holder, Edith

Subject: Oil Degradation Data- Dispersant project

Hi Mobing and Yu,

Could you please send your oil degradation data (normalized and non-normalized) in an excel format so that Jorge and group can continue working on their analysis.

Thanks,

Devi

Devi Sundaravadivelu, Ph.D.

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

(585) 732-4101 / (513) 569-7478

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Malcolm Gore
Sent: Mon 4/25/2016 3:19:05 PM
Subject: Re: Finasol OSR 52 Sample Request

OK Robyn. Will do.
Malcolm

Malcolm Gore
President

CLEAR COAST

+1 832 244 1533
malcolm.gore@clearcoastllc.com
www.clearcoastllc.com

From: "Conmy, Robyn" <Conmy.Robyn@epa.gov>
Date: Monday, April 25, 2016 at 10:05 AM
To: malcolm gore <malcolm.gore@clearcoastllc.com>
Cc: Peter Egan <peter.egan@total.com>
Subject: RE: Finasol OSR 52 Sample Request

Hello Malcolm,

Thank you for getting back with me regarding the purchase. Yes, the information below is
correct, with a mail stop at room 166. Can you send to me the invoice via email so I can provide
to the purchase card holder to make the purchase?

Thank you in advance,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Malcolm Gore [mailto:malcolm.gore@clearcoastllc.com]
Sent: Monday, April 25, 2016 10:57 AM
To: Conmy, Robyn <Conmy.Robyn@epa.gov>
Cc: Peter Egan <peter.egan@total.com>
Subject: Finasol OSR 52 Sample Request

Hello Robin

I am writing with respect to your email below regarding a sample request of Total Finasol OSR 52.

Clear Coast is the custodian of the product stored here in Houston for Total.

I will arrange the sample as requested.

Please confirm the following:

Contact:

Robyn Conmy 513-569-7090 (office)

Deliver to:

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

Quantity:

2 US Gallons.

On receipt of confirmation I will get the samples drawn, packaged and dispatched.

Regards

Malcolm

Malcolm Gore

President

CLEAR COAST

+1 832 244 1533

malcolm.gore@clearcoastllc.com

www.clearcoastllc.com

From: Conmy, Robyn
Sent: Monday, April 18, 2016 10:47 AM
To: 'peter.egan@total.com' <peter.egan@total.com>
Cc: Wilson, Gregory <Wilson.Gregory@epa.gov>; Principe, Vanessa <Principe.Vanessa@epa.gov>
Subject: purchase of Finasol OSR52

Mr. Egan,

This follows up our telephone conversation of April 11.

As discussed, EPA is seeking to acquire a number of dispersant products listed on the NCP Subpart J Product Schedule for the purposes of both toxicity and efficacy testing. The product testing is intended to further inform currently proposed regulatory actions under Subpart J of the National Contingency Plan. The products will in addition be used to support our general research in the area of oil spill response.

Your product Finasol OSR52 has been identified as one of interest, as it is commonly stockpiled in the U.S. Not only could the product be encountered when presented with a response situation, but including this dispersant product in toxicity and efficacy testing studies will also allow for comparison and consistency with other existing and ongoing studies by EPA and other federal agencies. EPA's Office of Research and Development (ORD) will be conducting the dispersant studies.

At this time we are seeking 2 U.S. gallons of the product.

We appreciate your time and attention to this request.

Respectfully,

Robyn Conmy

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

To: Mandsager, Kathy[kathy.mandsager@unh.edu]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]; fingasmerc@shaw.ca[fingasmerc@shaw.ca];
tchazen@utk.edu[tchazen@utk.edu]; robert.jones@noaa.gov[robert.jones@noaa.gov];
mandyjoye@gmail.com[mandyjoye@gmail.com]; ken.lee@csiro.au[ken.lee@csiro.au];
tracee.nguyen@csiro.au[tracee.nguyen@csiro.au]; mbleigh@alaska.edu[mbleigh@alaska.edu];
karl.linden@colorado.edu[karl.linden@colorado.edu]; kmmcfarlin@alaska.edu[kmmcfarlin@alaska.edu];
msmiles@lsu.edu[msmiles@lsu.edu];
thomas.s.coolbaugh@exxonmobil.com[thomas.s.coolbaugh@exxonmobil.com];
mathijs.smit@shell.com[mathijs.smit@shell.com]; Sprenger, Mark[Sprenger.Mark@epa.gov];
nancy.kinner@unh.edu[nancy.kinner@unh.edu]
From: Ian Gaudreau
Sent: Thur 7/9/2015 2:09:50 PM
Subject: Re: FW: Paper Addition to Degradation & Fate
Prince 2015 Oil Spill Dispersants Boon or Bane.pdf

Along with the Aeppli et al. 2014 and USGS paper, we need to discuss the Prince 2015 paper today (attached).

On Tue, Jun 30, 2015 at 1:44 PM, Mandsager, Kathy <kathy.mandsager@unh.edu> wrote:

Here is more information for the Degradation & Fate Group to review....

From: Ian Gaudreau [mailto:iangaudreau@gmail.com]
Sent: Tuesday, June 30, 2015 1:35 PM
To: Mandsager, Kathy
Subject: Paper Addition to Degradation & Fate

Hello everyone,

For the following statement in the Degradation & Fate document:

(line 311) However, there is a documented publication bias against null results.

We added a Fanelli 2014 reference from PLoS ONE. The paper is attached for your reference.

--

Ian Gaudreau

Environmental Engineering Graduate Student

University of New Hampshire

(978) 758-3561

iangaudreau@gmail.com

--
Ian Gaudreau

Environmental Engineering Graduate Student
University of New Hampshire
(978) 758-3561
iangaudreau@gmail.com

Oil Spill Dispersants: Boon or Bane?

Roger C. Prince*

ExxonMobil Biomedical Sciences, Inc., Annandale, New Jersey 08801 United States

Dispersants provide a reliable large-scale response to catastrophic oil spills that can be used when the preferable option of recapturing the oil cannot be achieved. By allowing even mild wave action to disperse floating oil into tiny droplets (<70 µm) in the water column, seabirds, reptiles, and mammals are protected from lethal oiling at the surface, and microbial biodegradation is dramatically increased. Recent work has clarified how dramatic this increase is likely to be: beached oil has an environmental residence of years, whereas dispersed oil has a half-life of weeks. Oil spill response operations endorse the concept of net environmental benefit, that any environmental costs imposed by a response technique must be outweighed by the likely benefits. This critical review discusses the potential environmental debits and credits from dispersant use and concludes that, in most cases, the potential environmental costs of adding these chemicals to a polluted area are likely outweighed by the much shorter residence time, and hence integrated environmental impact, of the spilled oil in the environment.
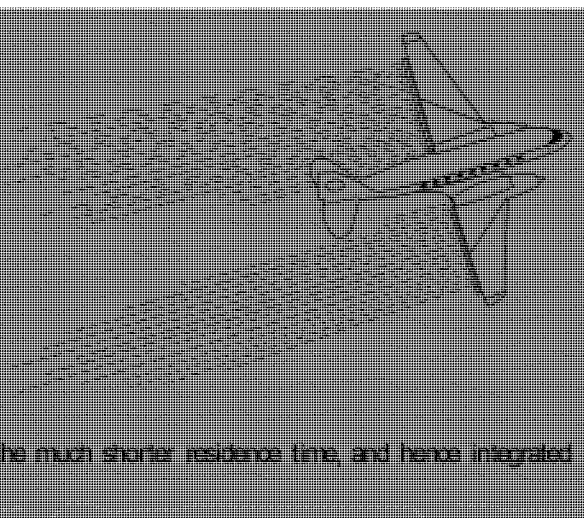
INTRODUCTION

Oil fuels our modern world, accounting for some 33% of energy consumption in 2013; daily consumption was 87 million barrels per day.[1] Some of this crude oil is produced from wells drilled under the sea, and a large percentage travels by sea between production and consumption. Despite the best efforts of the oil and shipping industries, some gets spilled. Catastrophic spills appropriately garner the public's attention, although, in fact, most spills are rather small. Natural seeps are likely the largest contributor of oil to the world's oceans, followed by nonpoint sources on land.[2] Tanker accidents are becoming less common,[3] but it is still true that a few large spills contribute the most oil released to the sea by ships, and where such spills occur, they release far more oil in a few days than even the most active seeps. The tragic 2010 blowout from the Deepwater Horizon well[4] is a reminder that large releases can also occur from drilling operations.

Crude oil has been part of the biosphere for millions of years,[5] and a large number of microbes, both prokaryotic[6] and eukaryotic,[7] have evolved to consume it. Biodegradation is the eventual fate for all spilled oil that is not collected or burned, and both collection and combustion require that spilled oil be corralled with booms.[8] While skimming can be an effective process if equipment is close to hand and the weather is reasonably calm, and is frequently part of oil spill response plans (e.g., refs 9–12), large spills in remote areas can spread so quickly that skimming becomes extremely difficult. For example, the Deepwater Horizon response, despite enormous efforts, collected only some 3% of the oil released and burned another 5%.[4] Considerable research has been expended, therefore, on trying to enhance the rate of oil biodegradation.

Oil is an unusual substrate for microbial growth for two distinct reasons. On the one hand, most oil molecules have low density and are very sparingly soluble, so oil tends to stay as surface slicks or droplets dispersed by wave action. Biodegradation is then limited by the surface area of the oil–water interface. On the other, whereas hydrocarbons are rich sources of carbon and energy, oil contains no other useful elements for microbial growth. Nitrogen and phosphorus are the most usual limiting nutrients in the sea,[13] followed by iron and other trace requirements.[14] While seawater contains trace levels of these nutrients,[15] the biodegradation of significant concentrations of oil, such as on a shoreline, is likely to exhaust the local supply. Bioremediation, the stimulation of biodegradation, thus aims to overcome these two limitations.

In the case of oil stranded on shorelines in Prince William Sound AK following the spill from the Exxon Valdez, the first response was to remove oil from beaches by washing it back to the sea and collecting it with skimmers.[16] This had the effect of leaving a relatively thin film of oil on the gravel and rocks of the intertidal (and sometimes supra-tidal) zone, and this was bioremediated by the careful addition of oleophilic and slow-release fertilizers to increase the supply of bioavailable nitrogen and phosphorus. This worked quite well, stimulating oil biodegradation between 2- and 5-fold without causing any additional adverse effects,[17−20] but it should be born in mind that the oil had already been on the shoreline for a year before the quantitative experiments reported therein were begun.

Floating oil presents different challenges. Floating oil is a very real hazard to diving birds and mammals (e.g., refs 21 and 22), and oil that beaches is a hazard to shorebirds,[23] invertebrates,[24,25] and mangroves.[26] Ameliorating these hazards was a primary impetus for the initial development of oil spill dispersants in the 1970s.[27] Modern dispersants are complex mixtures of anionic and neutral surfactants in a hydrocarbon solvent (e.g., ref 28) that lower the interfacial tension between oil and water so that minimal wave action and turbulence can disperse the oil into tiny droplets (<70 μm) in the water column. Such droplets are essentially neutrally buoyant, so with minimal turbulence they stay in the water column and diffuse apart. Concentrations of dispersed oil may be ≈1000 ppm in the first minutes after dispersion, but they fall to a few ppm, in a correspondingly larger volume, within hours, and to sub parts per million levels within a day.[29-34] Furthermore, even these concentrations are found only in the top few meters of the sea. Similarly, dispersants can harness the ejection turbulence of oil emanating from an uncontrolled subsea release and allow the formation of tiny oil droplets in the deep sea;[4,34-37] again, the droplets diffuse apart until they are in the sub parts per million concentration range. This diffusive dilution means that, although the levels of nutrients in the sea are relatively low,[13] it does not take long for oil concentrations to fall so that even those low levels are adequate for significant and rapid biodegradation. Hazen et al.[14,35] measured half-lives of n-alkanes of a few days in the dilute (2-442 ppb[34]) dispersed submarine plume from the Deepwater Horizon at 1100-1220 m (and 5 °C), and very similar results were reported for a broad array of individual hydrocarbons at low concentrations in New Jersey seawater at 8 °C,[36,37] in a flume in Trondheim, Norway,[38] at 30-32 °C and in water off the Penang, Malaysia, shore[39] at 27.5 °C. The approximate biodegradation half-life of the total measurable hydrocarbons was 11-14 days, both at low oil concentrations with indigenous nutrients[36,38] (2.5 and 43 ppm oil, respectively) and at slightly higher concentrations (100 ppm oil) with added nutrients.[39] Even the four ring aromatic chrysene and its methyl-, dimethyl-, and ethyl-alkylated forms had half-lives on the order of a month.[36]

DISPERSANTS

Dispersants have been used on a large scale in many responses, notably, the 1993 Braer wreck in the Shetland Islands,[40] the 1996 Sea Empress spill in South Wales,[41] and the 2010 Deepwater Horizon blowout in the Gulf of Mexico.[33] Seven spills in the US portion of the Gulf of Mexico were treated with dispersants between 1995 and 2004.[42] Dispersants are stockpiled, with equipment for their use, in large quantities around the world,[43] and substantial illustrated guidelines for their use are freely available.[44] Nevertheless, their deployment is still controversial, for clearly dispersants are not without potential drawbacks. Most dispersants are not themselves significantly toxic; they have toxicities indistinguishable from common household dish liquids and shampoos,[45] including those used for cleaning oiled seabirds,[46,47] and the majority, including those used in the Deepwater Horizon response, show neither androgen- nor estrogen-receptor activity.[48] Nevertheless, the use of dispersants involves adding more chemicals to an already impacted area, and the water under a recently dispersed oil slick is significantly transiently more toxic to organisms than under the undispersed slick, albeit because of the greater concentrations of oil in the water, not because of any increase in toxicity on an oil weight basis.[47,48,50]

So, how should spill response coordinators decide when and where to use dispersants? Most responders rely on a net environmental benefit analysis, often abbreviated NEBA.[51-55] At first glance, the concept seems oxymoronic: how can anything related to an oil spill have an environmental benefit? However, in actuality, the concept is very useful: everyone involved in a cleanup recognizes that an oil spill is a dreadful environmental insult and is working diligently to minimize adverse impacts and to remove the oil as quickly as possible. The question is whether a response tool will end up doing more harm than good, of whether there will be net environmental improvement despite potential collateral harm done in the short term by the response. Table 1 offers a comparison of the potential hazards and environmental fate of floating slicks and dispersed oils that need to be considered in such analyses.

The first hurdle for dispersants is to demonstrate their fundamental efficacy. In the United States, the U.S. Environmental Protection Agency (USEPA) maintains the National Oil and Hazardous Substances Pollution Contingency Plan Product Schedule[56] as part of the National Contingency Plan and lists chemical dispersants that may be authorized for use. Dispersants on the Product Schedule have demonstrated effectiveness; they can disperse at least 45% of Prudhoe Bay or South Louisiana crude oil in a standard swirling flask test.[57] The swirling flask test is one of several tests designed to discriminate between dispersants with different efficacies on a simple laboratory scale. It does this reasonably well (although the USEPA is considering revising it with a baffled flask test[58]), but unfortunately the passing grade of 45% has often been assumed to indicate expected field performance. In fact, the test dramatically underestimates efficacy in the field, primarily due to the amount of energy it imparts to the floating oil and the volume available for diffusion. Tests in the OHMSETT facility,[59] a wave tank in New Jersey that is 200 m long, 20 m wide, and 2.5 m deep, routinely measure dispersant efficiencies >95%, even at low temperatures with ice in the water.[60]

A second requirement for listing on the USEPA product schedule is that the acute toxicity of the dispersant to two reference species (silverside fish, Menidia beryllina (96 h), and mysid shrimp, Americamysis bahia (48 h)[49,59]) be reported. During the Deepwater Horizon response, the USEPA required that dispersants "have a toxicity value less than or equal to (sic) 23.00 (sic) ppm LC_{50} toxicity value for Menidia or 18.00 ppm LC_{50} for Mysidopsis (Americamysis)";[62] the dispersants being used passed this hurdle.[49]

As mentioned above, the toxicity of modern dispersants is usually so low as to likely have only minimal adverse effects at levels used in response operations (nominal aerial dispersant application rates are 5 gallons of dispersant per acre, 47 L/hectare;[63] diffusion into the top 20 cm of seawater would give concentrations around 23 ppm, and of course further diffusion will continually lower the concentration). However, dispersed oil is significantly more toxic, with acute LC_{50} values more than an order of magnitude lower.[49] There has been some confusion around quantifying the toxicity of dispersed oil;[64,65] acute toxicity arises from a general narcosis caused by dissolved hydrocarbons moving to the lipids of the test organism,[66-68] so if estimates of oil concentrations include small droplets, the toxicity expressed on a per milligram hydrocarbon basis are lower (higher LC_{50}) than that for dissolved components. In any case, dispersants encourage solubility by increasing the surface-

Table 1

potential hazards and environmental fate of dispersants and dispersed oil

Dispersant application has the potential to create aerosols with potentially adverse effects on humans and wildlife. Such effects are seen only in the laboratory at quite high concentrations and with prolonged exposures.[99-102] They are minimized by protective equipment for applicators and exclusion zones around application. Aerial application is very unlikely to be approved within several miles of a coast.

The addition of dispersants puts additional chemicals into a polluted area. Nominal application rates of dispersants are 5 gallons per acre (47 L ha^{-1}) for surface spills,[63] equivalent to a dispersant/oil ratio of about 1:20. Subsea injection seems to be effective at a much lower doses, perhaps 1:100 or less. Dispersants are composed of chemicals that are generally acceptable for food contact and are biodegradable,[23,93,94] but when they are used at suboptimal doses, they may become incorporated into persistent tarballs.[95]

Dispersants may persist in the environment. Dispersants are complex mixtures of surfactants and solvents, and very few techniques can measure them all.[104] Much published work has focused on individual chemicals, but since all of the components are widely used in consumer products on a far greater scale than in dispersants, care must be taken in attributing detection to dispersant use.[97]

Dispersants may not penetrate heavy oils and may "roll-off" before they can be effective.[103,105] Nevertheless, dispersants have been shown to be effective with many heavy oils,[117] and new formulations are being developed to further this use.[106]

Suboptimal dispersant application may not disperse the oil but may hinder subsequent skimming operations.

Several studies appear to show that dispersants do not stimulate biodegradation very much.[139-141,36,78] Those experiments were based on a misunderstanding of the role of dispersants,[37] which is simply to disperse oil into tiny droplets that can diffuse apart. Such dilute small droplets, whether generated by dispersants or by low concentrations of oil, are degraded rapidly,[35-38,78] and dispersants show no significant stimulatory effect. Dispersed oils that can recoalesce into larger droplets, as occurs in laboratory experiments with more than a few parts per million oil,[139-141] again show only a small stimulation of biodegradation by dispersants. A clear stimulation of biodegradation by dispersants (many fold) is seen only when dispersed oil at environmentally realistic concentrations[29-38] is compared to an undispersed slick.[37] It is the latter that is the target of dispersants.

Dispersants have been reported to be toxic to some bacteria.[142] These experiments looked at a few isolated cultivars from beach sand rather than pelagic organisms likely to be exposed to dispersants. Dispersants had no inhibitory effects in experiments with pelagic microbes[36-38,78] and were significantly less toxic than oil alone to Vibrio fischeri (now Aliivibrio fischeri[143].) in the Microtox test.[144]

Dispersed oil is potentially toxic to organisms close to the surface when the oil is initially dispersed. This is particularly true for small invertebrates, algae, fish eggs, and young that cannot swim away.[109] Nevertheless, measured dilution suggests that they will not be exposed for very long.[29-36] The remarkably heterogeneous distribution of planktonic organisms on all scales, probably has more influence on local populations than relatively small-scale mortality due to concentrated dispersions of oil.[145,146] Planktonic microbial species respond remarkably rapidly, even to diel cycles.[147] Fish kills are rarely noted after dispersant use, presumably because fish and other nekton swim away from the dispersed oil.

Dispersed polycyclic aromatic compounds may be accumulated by transparent planktonic organisms, which may then be subject to phototoxicity in the surface layer of the sea.[113]

Dispersion slows evaporation, especially if the oil is dispersed subsea, as some was in the Deepwater Horizon response. The potentially toxic small molecules are retained in the water column until they are biodegraded or escape to the atmosphere over a much greater area due to diffusion at depth.

Dispersants are typically used far from shore in deep water (e.g., >3 miles[148].) Dispersed oil diffuses to sub parts per million levels and is very unlikely to reach a shoreline in noticeable quantities.

Dispersed oil dilutes to such low concentrations that biodegradation is rapid. Measured half-lives are in the days to few weeks time frame.[14,33-37] Even the four ring aromatic chrysene and its methyl-, dimethyl-, and ethyl- forms have half-lives on the order of a month.[36] Nearshore waters from the Chukchi Sea,[78] the North West Atlantic,[36] and deepwater from Trondheim Fjord[38] all contained enough nutrients for substantial biodegradation of a few parts per million oil in 60 days, and it is reasonable to extrapolate that further dilution in more oligotrophic waters would allow similar degradation on similar time scales.

potential hazards and environmental fate of floating slick

Floating oil can be lethal to birds or mammals that penetrate it. The oil reduces the insulating properties of feathers and fur and may be toxic if ingested during preening or grooming.[2,12] Mild oiling may be transferred to eggs, chicks, and young.[107] Floating oil also likely kills small invertebrates, algae, fish eggs, and young that are at the sea surface under the slick.[108]

Floating oil is subject to photooxidation, which polymerizes polycyclic aromatic compounds to polar materials.[110,111] This eventually leads to very persistent tarballs.[112] Beached oil undergoes a similar process, leading to very persistent "pavements".[126,127]

Transparent planktonic organisms may accumulate polycyclic aromatic compounds leached from slicks and beached oil and may be subject to phototoxicity in the surface layer of the sea.[113]

Floating oil absorbs water; it is not unusual for floating slicks to increase their volume by >50% in 24 h.[114-116] This phenomenon makes dispersion more difficult but not impossible.[117] Over several days, many floating oils emulsify, forming water-in-oil emulsions known as mousse.[118-120] The encapsulated water no longer exchanges with bulk seawater, and biodegradation is likely even more nutrient- and oxygen-limited than in the floating slick. Mousse may be consumed by fish, turtles, etc. and also lead to tarballs.[131,132]

Small molecules in floating oil evaporate rapidly, becoming volatile organic compounds (VOCs)[119,120] that can reach levels of concern for spill responders.[121] Evaporated molecules may be destroyed by photochemistry[122] or biodegradation.[123]

If it is not physically dispersed by storms or recovered mechanically, then an oil slick will likely beach on a shoreline. If it stays on the shoreline surface, then it may be possible to remove it by physical means, but storms will likely incorporate oil deep into sandy beaches,[124,125] where, if left alone, it will likely remain for decades.[126,127] Beached oil can be a major threat to turtle and shorebird nesting[128] and to mangroves[130] and marshes,[130] and recovery may take years.[131,132]

If the slick arrives at a shoreline, then biodegradation will be slow because of the high concentration of oil in comparison to the low concentrations of bioavailable nutrients in tidal flows. Biodegradation was too slow to measure directly,[18,19] in the absence of bioremediation in Prince William Sound following the Exxon Valdez spill,[18,19] but even with effective bioremediation, the half-life of total detectable hydrocarbons was of the order of 10 weeks.[18,19] The

ED_001324_00000389-00003

Table 1. continued

| potential hazards and environmental fate of floating slick	potential hazards and environmental fate of dispersants and dispersed oil
biodegradation of bulk oil in the Gulf of Mexico was very slow[74,75] compared to that of dispersed oil.[35,14]	
While oil hydrocarbons are essentially completely biodegradable (e.g., ref 36), many of the deeply colored molecules (resins, asphaltenes, polars, etc.) are more resistant to biodegradation, although at least some are consumed.[133,134] While these have minimal biological effects, the lifetime of these molecules in a sandy beach may be prolonged, especially if they have been entrained deep in a beach by storm action.[124,132]	While oil hydrocarbons are essentially completely biodegradable (e.g., ref 36), many of the deeply colored molecules (resins, asphaltenes, polars, etc.) are more resistant to biodegradation, although at least some are consumed.[133,134] Once the hydrocarbons have been degraded, these fractions lack oily characteristics and become essentially indistinguishable from other inert organic matter in the environment, such as humins.[133]
Physical cleanup of beached oil can take weeks to years and requires hundreds to thousands of workers with their ancillary vehicles and support services[16,128,136]	Optimal dispersant application for surface slicks uses planes that can carry 5000 gallons (19000 L) of dispersant, appropriate to treat 1000 acres (405 ha) of slick.[63] Depending on distances from airfields, several sorties can be flown per day, and spills from a tanker can be treated in a few days. Aerial spraying requires daylight (Figure 1).
	Subsea injection has the advantage of continuing 24 h a day, and the lower application rates mean that dispersant stocks will potentially last longer. If fully successful, oil from a subsea release may never reach the surface before it is biodegraded.[103]
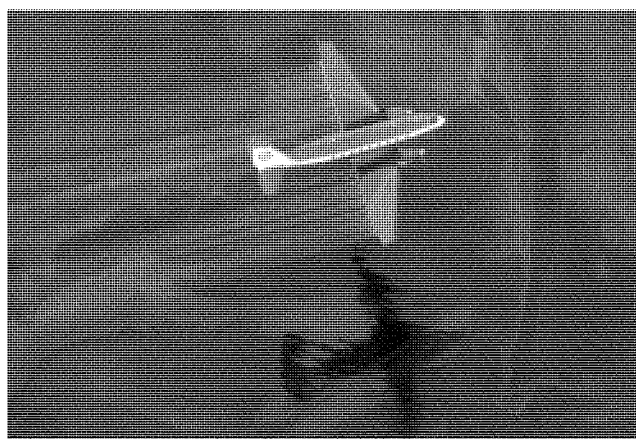
Figure 1. An updated DC3C spraying dispersants on oil from the Deepwater Horizon blowout. The wingspan is 29 m. Reproduced with permission from Airborne Support.

to-volume ratio of the oil, and there is a potential for short-term toxic effects in a dispersed plume. The question is how significant these effects might be in the field. Canonical acute toxicity tests involve constant exposures for 48 or 96 h,[61] but in a response at sea, the concentrations of oil will be dropping rapidly due to dilution by mixing and diffusion. As noted above, concentrations of dispersed oil drop to below 1 ppm within a few hours.[29-33]

Only acute toxicity tests are required for listing under the National Contingency Plan, but of course chronic effects are also a real concern. As expected, the longer exposure required to see chronic effects allows lower concentrations of hydrocarbons to exert an effect, and typical acute-to-chronic ratios are 1:10, that is, it may only take 10% of the acute LC_{50} to have a chronic EC_{50}.[69-72] Again, these concentrations are for prolonged exposures, and it is not clear how these relate to the very low concentrations[29-34] of dispersed oil that are found several days after dispersion.[73]

As noted at the outset, dispersants were initially conceived as a tool for minimizing seabird mortality, and early use weighed that benefit against potential toxicity to planktonic species.[27] However, an additional substantial benefit has now been clearly documented: the biodegradation of dispersed oil is dramatically faster than that of oil in a slick or on a shoreline. Oil on shorelines of Prince William Sound, Alaska, had a half-life of a year or more,[18-20] even with the substantial washing and bioremediation program.[16] Tarballs and mousse associated with the Deepwater Horizon blowout had similar persistence in the environment.[74,75] However, the biodegradation of dispersed oil is rapid and extensive.[14,35-37]

The oil spill response community agrees that the best response to an oil spill would be to collect it from the environment before it reached a shoreline, and many response plans focus on this requirement by staging large amounts of equipment aimed at achieving this goal even in the face of a very large spill (e.g., refs 9-12). However, if oil cannot be collected, particularly if it is unsafe for responders to perform mechanical recovery or because of remote location or hours of daylight, then responders must look to other methods. It is important to recognize that time is of the essence: deciding not to use a response option today may preclude its use tomorrow. This phenomenon, the window-of-opportunity,[76] is particularly relevant to the use of dispersants because as oil weathers by

evaporation and absorption of underlying water, it becomes progressively more and more difficult to disperse with dispersants. (As an aside, dispersants incorporated into relatively fresh oil will help the dispersion of that oil even after some time if conditions are initially too calm for immediate dispersion,[77] a potential problem for requirements that dispersants be seen to be effective on a trial basis before large-scale application can begin.) Responders must weigh the potential additional short-term toxicity likely incurred immediately under a dispersed surface slick against the benefit of protecting diving birds and animals and having the oil removed from the environment by biodegradation on a time scale of a few weeks rather than years with a vastly smaller human footprint of spill response. The speed of biodegradation is particularly important if the over-riding concern about dispersant use is the potential local increase in toxicity; beached oil and undispersed mousse leach hydrocarbons and have their own potential environmental impacts for a prolonged period. It would also be prudent to bear in mind the environmental impact of large shoreline cleanup operations, which often involve hundreds of workers and the ancillary impacts of their support services. There is also the potential legacy of the final disposal of the oil, which may well involve burial at a secure landfill rather than combustion or biodegradation. Finally, while not an environmental impact, the economic impacts of an oiled marina or shoreline also need to be weighed as responders decide the most appropriate spill-response.

CONCLUDING REMARKS

In the final analysis, some accidents occur so close to shore that oil will undoubtedly reach the shoreline and most likely require some physical cleanup, perhaps followed by bioremediation. However, if the release is in deep water, then it ought to be possible to mobilize dispersants to keep bulk oil from ever reaching a shoreline. If oil is successfully dispersed into the water column, then it is likely that biodegradation will remove the vast majority of it in weeks to months, even in the Arctic and Antarctic.[78] What remains will likely be finely dispersed fragments of nonoily (to the touch) material depleted of hydrocarbons and rich in asphaltic materials and saturated biomarkers such as the hopanes.[36,79,80]

Many questions remain to be answered:

How does the density of dispersed oil change as biodegradation proceeds? Alkanes are much lighter than water,[81] even at high pressure,[82] as are cyclic alkanes and monoaromatics. However, larger aromatic hydrocarbons, such as chrysene, have densities greater than 1,[83] as do the resins and asphaltenes.[84,85] Since biodegradation preferentially removes alkanes, initially buoyant droplets will become neutral and eventually sink. Is this partially degraded oil further metabolized once deposited on the surface sediment at depth? Reports of substantial amounts of fossil (radiocarbon silent) carbon on the surface sediment at depth[86] could be either unmetabolized oil molecules or the biomass of organisms degrading the oil or, more likely, both. As noted above, some molecules, such as the hopanes, seem very resistant to biodegradation and likely remain with very biodegraded oil (and degrading biomass) as a fingerprint of the initial source.[36,75,79,80]

What fraction of the oil carbon is mineralized to CO_2 in the initial biodegradation, and what fraction is incorporated into biomass? Classical experiments with aerobes growing on glucose suggest a biomass yield of about 50%,[87] but what is the fate of that biomass? Levy and Lee[88] propose that it is the base for substantial fisheries offshore Atlantic Canada. Chemical analysis of the radiocarbon silent material reported by Chanton et al.[86] will shed light on this question.

What role does microbial succession play in the biodegradation of oil? Such succession was clearly seen in the Gulf of Mexico following the Deepwater Horizon release,[87–92] but how did it relate to the chemical composition of the residual oil or to the nutrient levels in the water? Do dispersants affect this succession?

How rapidly are dispersant components degraded in the sea? Early work established the biodegradation of nonionic surfactants in seawater,[93] and dioctylsulfosuccinate is known to be biodegradable[94] and clearly was being degraded close to the Deepwater Horizon spill site where it was being applied in the Corexit dispersant.[95] Nevertheless, traces of dioctylsulfosuccinate have been found far from the Deepwater Horizon accident;[96] was that associated with dispersant application? Traces found close to shore are more likely related to stormwater discharges.[95] Small quantities associated with tarballs[98] are likely the result of suboptimal dispersant application and highlight the need to apply an effective amount of dispersant if its benefits are to be achieved.

Is biodegradation at depth (>1500 m) fundamentally distinct from biodegradation at the surface? Early work suggested that it is not,[137] but that work was clearly limited in its experimental tools, and there is much to learn. There is no doubt that active hydrocarbon-degrading microbial communities, both aerobic and anaerobic, are present in deep sea sediments.[138]

Already, however, we know enough from laboratory, mesocosm, and field experience to say that dispersed oil is degraded much more rapidly than undispersed oil, likely orders of magnitude more rapidly. This is the key piece of information that seems to be overlooked in most discussions of the potential adverse impacts of using dispersants. Even if there is an adverse local impact of dispersed oil, it will not last long. On the other hand, oil that reaches a shoreline may be there for years.

AUTHOR INFORMATION

Corresponding Author
*E-mail: roger.c.prince@exxonmobil.com. Phone: 908 730 2134. Fax: 908 730 1199.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Statistical Review of World Energy; BP, 2014. http://www.bp.com/en/global/corporate/about-bp/energy-economics/statistical-review-of-world-energy.html.

(2) National Research Council Oil in the Sea III: Inputs, Fates, and Effects; National Academies Press: Washington, DC, 2003.

(3) Musk, S. Trends in oil spills from tankers and ITOPF non-tanker attended incidents, 2012. http://www.itopf.com/knowledge-resources/documents-guides/document/trends-in-oil-spills-from-tankers-and-itopf-non-tanker-attended-incidents-2012/.

(4) Lubchenco, J.; McNutt, M. K.; Dreyfus, G.; Murawski, S. A.; Kennedy, D. M.; Anastas, P. T.; Chu, S.; Hunter, T. Science in support of the Deepwater Horizon response. Proc. Natl. Acad. Sci. U.S.A. 2012, 109, 20212−20221.

(5) Tissot, B. P.; Welte, D. H. Petroleum Formation and Occurrence; Springer: Berlin, 1984.

(6) Prince, R. C.; Gramain, A.; McGenity, T. J. Prokaryotic hydrocarbon degraders. In Handbook of Hydrocarbon and Lipid Microbiology; Timmis, K. N., Ed.; Springer-Verlag: Berlin, 2010; pp 1672−1692.

(7) Prince, R. C. Eukaryotic hydrocarbon degraders. In Handbook of Hydrocarbon and Lipid Microbiology; Timmis, K. N., Ed.; Springer-Verlag: Berlin, 2010; pp 2066−2078.

(8) Fingas, M. The Basics of Oil Spill Cleanup; CRC Press: Boca Raton, FL, 2012.

(9) Alyeska Oil Spill Prevention, Response and Preparedness, 2014. http://www.alyeska-pipe.com/SafetyEnvironment/PreventionAndResponse.

(10) San Francisco Oil Spill Contingency Plan, 2014. https://www.dfg.ca.gov/ospr/san_francisco_plan.aspx.

(11) Thames Oil Spill Clearance Association, 2014. http://www.pla.co.uk/About-Us/TOSCA.

(12) ITOPF Country Profiles, 2014. http://www.itopf.com/knowledge-resources/countries-regions/.

(13) Atlas, R. M.; Bartha, R. Degradation and mineralization of petroleum in sea water: limitation by nitrogen and phosphorus. Biotechnol. Bioengineer. 1972, 14, 309−318.

(14) Baelum, J.; Borglin, S.; Chakraborty, R.; Fortney, J. L.; Lamendella, R.; Mason, O. U.; Auer, M.; Zemla, M.; Bill, M.; Conrad, M. E.; Malfatti, S. A.; Tringe, S. G.; Holman, H. Y.; Hazen, T. C.; Jansson, J. K. Deep-sea bacteria enriched by oil and dispersant from the Deepwater Horizon spill. Environ. Microbiol. 2012, 14, 2405−2416.

(15) Garcia, H. E.; Locarnini, R. A.; Boyer, T. P.; Antonov, J. I.; Zweng, M. M.; Baranova, O. K.; Johnson, D. R. World Ocean Atlas 2009: Nutrients (Phosphate, Nitrate, And Silicate), NOAA Atlas NESDIS 71; Levitus, S., Ed.; U.S. Government Printing Office: Washington, DC, 2010; Vol. 4.

(16) Nauman, S. A. Shoreline cleanup: equipment and operations. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1991; pp 141−147.

(17) Lindstrom, J. E.; Prince, R. C.; Clark, J. R.; Grossman, M. J.; Yeager, T. R.; Braddock, J. F.; Brown, E. J. Microbial populations and hydrocarbon biodegradation potentials in fertilized shoreline sediments affected by the T/V Exxon Valdez oil spill. Appl. Environ. Microbiol. 1991, 57, 2514−2522.

(18) Bragg, J. R.; Prince, R. C.; Harner, E. J.; Atlas, R. M. Effectiveness of bioremediation for the Exxon Valdez oil spill. Nature 1994, 368, 413−418.

(19) Prince, R. C.; Clark, J. R.; Lindstrom, J. E.; Butler, E. L.; Brown, E. J.; Winter, G.; Grossman, M. J.; Parrish, R. R.; Bare, R. E.; Braddock, J. F.; Steinhauer, W. G.; Douglas, G. S.; Kennedy, J. M.; Barter, P. J.; Bragg, J. R.; Harner, E. J.; Atlas, R. M. Bioremediation of the Exxon Valdez oil spill: monitoring safety and efficacy. In Hydrocarbon Remediation; Hinchee, R. E., Alleman, B. C., Hoeppel, R. E., Miller, R. N., Eds.; Lewis Publishers: Boca Raton, FL, 1994; pp 107−124.

(20) Prince, R. C.; Bragg, J. R. Shoreline bioremediation following the Exxon Valdez oil spill in Alaska. Biorem. J. 1997, 1, 97−104.

(21) Page, G. W.; Carter, H. R.; Ford, R. G. Numbers of seabirds killed or debilitated in the 1986 Apex Houston oil spill in central California. Studies Avian Biol. 1990, 14, 164−174.

(22) Murphy, S. M.; Day, R. H.; Wiens, J. A.; Parker, K. R. Effects of the Exxon Valdez oil spill on birds: comparisons of pre-and post-spill surveys in Prince William Sound, Alaska. Condor 1997, 99, 299−313.

(23) Henkel, J. R.; Sigel, B. J.; Taylor, C. M. Large-scale impacts of the Deepwater Horizon oil spill: can local disturbance affect distant ecosystems through migratory shorebirds? BioScience 2012, 62, 676−685.

(24) Chasse, C. The ecological impact on and near shores by the Amoco Cadiz oil spill. Mar. Pollut. Bull. 1978, 9, 298−301.

(25) Neuparth, T.; Moreira, S. M.; Santos, M. M.; Reis-Henriques, M. A. Review of oil and HNS accidental spills in Europe: identifying major environmental monitoring gaps and drawing priorities. Mar. Pollut. Bull. 2012, 64, 1085−1095.

(26) Anink, P. J.; Hunt, D. R.; Roberts, D. E.; Jacobs, N. E. Oil spill in Botany Bay: short term effects and long term implications. Wetlands (Australia) 1985, 5, 32−41.

(27) National Research Council Oil Spill Dispersants: Efficacy and Effects; National Academy Press: Washingon, DC, 2005.

(28) COREXIT® Ingredients; Nalco: Sugar Land, TX, 2014. http://www.nalcoesllc.com/nes/1602.htm.

(29) Cormack, D.; Nichols, J. A. The concentrations of oil in sea water resulting from natural and chemically induced dispersion of oil slicks. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1977; pp 381−385.

(30) Lichtenthaler, R. G.; Daling, P. S. Dispersion of chemically treated crude oil in Norwegian offshore waters. In International Oil Spill Conference; American Petroleum Institute: Washington, DC, 1983; pp 7−14.

(31) McAuliffe, C. D.; Johnson, J. C.; Greene, S. H.; Canevari, G. P.; Searl, T. D. Dispersion and weathering of chemically treated crude oils on the ocean. Environ. Sci. Technol. 1980, 14, 1509−1518.

(32) BenKinney, M.; Brown, J.; Mudge, S.; Russell, M.; Nevin, A.; Huber, C. Monitoring effects of aerial dispersant application during the MC252 Deepwater Horizon Incident. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 2011; p 368.

(33) Bejarano, A. C.; Levine, E.; Mearns, A. J. Effectiveness and potential ecological effects of offshore surface dispersant use during the Deepwater Horizon oil spill: a retrospective analysis of monitoring data. Environ. Monit. Assess. 2013, 185, 10281−10295.

(34) Wade, T. L.; Sweet, S. T.; Sericano, J. L.; Guinasso, N. L.; Diercks, A. R.; Highsmith, R. C.; Asper, V. L.; Joung, D. J.; Shiller, A. M.; Lohrenz, S. E.; Joye, S. B. Analyses of water samples from the Deepwater Horizon oil spill: documentation of the subsurface plume. In Monitoring and Modeling the Deepwater Horizon Oil Spill: A Record-Breaking Enterprise; Liu, Y., Macfadyen, A., Ji, Z. J., Weisberg, R. H., Eds; American Geophysical Union: Washington, DC, 2011; pp 77−82.

(35) Hazen, T. C.; Dubinsky, E. A.; DeSantis, T. Z.; Andersen, G. L.; Piceno, Y. M.; Singh, N.; Jansson, J. K.; Probst, A.; Borglin, S. E.; Fortney, J. L.; Stringfellow, W. T.; Bill, M.; Conrad, M. S.; Tom, L. M.; Chavarria, K. L.; Alusi, T. R.; Lamendella, R.; Joyner, D. C.; Spier, C.; Baelum, J.; Auer, M.; Zemla, M. L.; Chakraborty, R.; Sonnenthal, E. L.; D'haeseleer, P.; Holman, H. N.; Osman, S.; Lu, Z.; Van Nostrand, J. D.; Deng, Y.; Zhou, J.; Mason, O. U. Deep-sea oil plume enriches indigenous oil-degrading bacteria. Science 2010, 330, 204−208.

(36) Prince, R. C.; McFarlin, K. M.; Butler, J. D.; Febbo, E. J.; Wang, F. C. Y.; Nedwed, T. J. The primary biodegradation of dispersed crude oil in the sea. Chemosphere 2013, 90, 521−526.

(37) Prince, R. C.; Butler, J. D. A protocol for assessing the effectiveness of oil spill dispersants in stimulating the biodegradation of oil. Environ. Sci. Pollut. Res. 2014, 21, 9506−9510.

(38) Brakstad, O. G.; Nordtug, T.; Throne-Holst, M. Biodegradation of dispersed Macondo oil in seawater at low temperature and different oil droplet sizes. Mar. Pollut. Bull. 2015, 93, 144−152.

(39) Zahed, M. A.; Aziz, H. A.; Isa, M. H.; Mohajeri, L.; Mohajeri, S.; Kutty, S. R. M. Kinetic modeling and half-life study on bioremediation of crude oil dispersed by Corexit 9500. J. Hazard. Mater. 2011, 185, 1027−1031.

(40) Harris, C. The Braer incident: Shetland Islands, January 1993. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1995; pp 813−819.

(41) Law, R. J.; Kelly, C. The impact of the Sea Empress oil spill. Aquat. Living Resour. 2004, 17, 389−394.

(42) Henry, C. Review of dispersant use in US Gulf of Mexico waters since the Oil Pollution Act of 1990. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 2005; pp 439−442.

(43) Global Dispersant Stockpile; Oil Spill Response Ltd.: London, 2014. http://www.oilspillresponse.com/services-landing/global-dispersant-stockpile.

(44) ExxonMobil Oil Spill Dispersant Guidelines, 2008. crrc.unh.edu/sites/crrc.unh.edu/files/exxonmobil_dispersant_guidelines_2008.pdf.

(45) Word, J. Q.; Clark, J. R.; Word, L. S. Comparison of the acute toxicity of Corexit 9500 and household cleaning products. Hum. Ecol. Risk Assess. 2014, 21, 707−725.

(46) Russell, M.; Holcomb, J.; Berkner, A. 30-years of oiled wildlife response statistics, Proceedings of the 7th International Effects of Oil on Wildlife Conference, Hamburg, Germany, October 14−16, 2003; pp 14−16. pszshhw.bird-rescue.org/pdfs/IBRRC_stats_paper.pdf.

(47) Best Practices for Migratory Bird Care During Oil Spill Response; USWFS: Anchorage, AK, 2003. www.fws.gov/contaminants/fws_oscp_05/fwscontingencyappendices/D-BestPracticesMigBirds/BestPracticesmar04rev.pdf.

(48) Judson, R. S.; Martin, M. T.; Reif, D. M.; Houck, K. A.; Knudsen, T. B.; Rotroff, D. M.; Xia, M.; Sakamuru, S.; Huang, R.; Shinn, P.; Austin, C. P.; Kavlock, R. J.; Dix, D. J. Analysis of eight oil spill dispersants using rapid, in vitro tests for endocrine and other biological activity. Environ. Sci. Technol. 2010, 44, 5979−5985.

(49) Hemmer, M. J.; Barron, M. G.; Greene, R. M. Comparative toxicity of eight oil dispersants, Louisiana sweet crude oil (LSC), and chemically dispersed LSC to two aquatic test species. Environ. Toxicol. Chem. 2011, 30, 2244−2252.

(50) Gardiner, W. W.; Word, J. Q.; Word, J. D.; Perkins, R. A.; McFarlin, K. M.; Hester, B. W.; Word, L. S.; Ray, C. M. The acute toxicity of chemically and physically dispersed crude oil to key arctic species under arctic conditions during the open water season. Environ. Toxicol. Chem. 2013, 32, 2284−2300.

(51) Baker, J. M. Net environmental benefit analysis for oil spill response. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1995; pp 611−614.

(52) Chapman, H.; Purnell, K.; Law, R. J.; Kirby, M. F. The use of chemical dispersants to combat oil spills at sea: a review of practice and research needs in Europe. Mar. Pollut. Bull. 2007, 54, 827−838.

(53) Kirby, M. F.; Law, R. J. Oil spill treatment products approval: the UK approach and potential application to the Gulf region. Mar. Pollut. Bull. 2008, 56, 1243−1247.

(54) API Net Environmental Benefit Analysis for Effective Oil Spill Preparedness and Response, 2013. www.api.org/~/media/Files/EHS/Clean_Water/Oil_Spill_Prevention/NEBA/NEBA-Net-Environmental-Benefit-Analysis-July-2013.pdf.

(55) McCay, D. F.; Graham, E. Quantifying tradeoffs-net environmental benefits of dispersant use. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 2014; pp 762−775.

(56) USEPA Alphabetical List of NCP Product Schedule (Products Available for Use During an Oil Spill), 2014 http://www2.epa.gov/emergency-response/alphabetical-list-ncp-product-schedule-products-available-use-during-oil-spill.

(57) USEPA Swirling Flask Dispersant Effectiveness Test, Revised Standard Dispersant Toxicity Test, and Bioremediation Agent Effectiveness Test, 2006. http://www.gpo.gov/fdsys/pkg/CFR-2006-title40-vol27/xml/CFR-2006-title40-vol27-part300-appC.xml.

(58) USEPA National Oil and Hazardous Substances Pollution Contingency Plan: Proposed Rule, 2015. https://www.federalregister.gov/articles/2015/01/22/2015-00544/national-oil-and-hazardous-substances-pollution-contingency-plan.

(59) Ohmsett · National Oil Spill Response Research Facility; BSSE: Washington, DC, 2014. http://www.bsee.gov/Technology-and-Research/Ohmsett/index/.

(60) Belore, R. C.; Trudel, K.; Mullin, J. V.; Guarino, A. Large-scale cold water dispersant effectiveness experiments with Alaskan crude oils and Corexit 9500 and 9527 dispersants. Mar. Pollut. Bull. 2009, 58, 118−128.

(61) Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 5th ed.; USEPA: Washington, DC, 2002. http://water.epa.gov/scitech/methods/cwa/wet/disk2_index.cfm.

(62) Dispersant Monitoring and Assessment Directive − Addendum; USEPA: Washington, DC, 2010. http://www.epa.gov/bpspill/dispersants/directive-addendum2.pdf.

(63) Dispersant Aerial Application Systems: Airborne Support Incorporated; Clean Gulf Associates: New Orleans, LA, 2014. http://www.cleangulfassoc.com/equipment/all/dispersant-aerial-application.

(64) Coelho, G.; Clark, J.; Aurand, D. Toxicity testing of dispersed oil requires adherence to standardized protocols to assess potential real world effects. Environ. Pollut. 2013, 177, 185−188.

(65) Lewis, M. M.; Pryor, R. Toxicities of oils, dispersants and dispersed oils to algae and aquatic plants: Review and database value to resource sustainability. Environ. Pollut. 2013, 180, 345−367.

(66) McGrath, J. A.; Parkerton, T. F.; Hellweger, F. L.; Di Toro, D. M. Validation of the narcosis target lipid model for petroleum products: gasoline as a case study. Environ. Toxicol. Chem. 2005, 24, 2382−2394.

(67) Di Toro, D. M.; McGrath, J. A.; Stubblefield, W. A. Predicting the toxicity of neat and weathered crude oil: Toxic potential and the toxicity of saturated mixtures. Environ. Toxicol. Chem. 2007, 26, 24-36.

(68) McCarty, L. S.; Arnot, J. A.; Mackay, D. Evaluation of critical body residue data for acute narcosis in aquatic organisms. Environ. Toxicol. Chem. 2013, 32, 2301−2314.

(69) Länge, R. R.; Hutchinson, T. H.; Scholz, N.; Solbe, J. Analysis of the ECETOC aquatic toxicity (EAT) database II · comparison of acute to chronic ratios for various aquatic organisms and chemical substances. Chemosphere 1998, 36, 115−127.

(70) Roex, E. W.; Van Gestel, C. A.; Van Wezel, A. P.; Van Straalen, N. M. Ratios between acute aquatic toxicity and effects on population growth rates in relation to toxicant mode of action. Environ. Toxicol. Chem. 2000, 19, 685−693.

(71) Raimondo, S.; Montague, B. J.; Barron, M. G. Determinants of variability in acute to chronic toxicity ratios for aquatic invertebrates and fish. Environ. Toxicol. Chem. 2007, 26, 2019−2023.

(72) Swigert, J. P.; Lee, C.; Wong, D. C. L; Podhasky, P. Aquatic hazard and biodegradability of light and middle atmospheric distillate petroleum streams. Chemosphere 2014, 108, 1−9.

(73) Landrum, P. F.; Chapman, P. M.; Neff, J.; Page, D. S. Influence of exposure and toxicokinetics on measures of aquatic toxicity for organic contaminants: a case study review. Integr. Environ. Assess. Manage. 2013, 9, 196−210.

(74) Aeppli, C.; Nelson, R. K.; Radovic, J. R.; Carmichael, C. A.; Valentine, D. L.; Reddy, C. M. Recalcitrance and degradation of petroleum biomarkers upon abiotic and biotic natural weathering of Deepwater Horizon oil. Environ. Sci. Technol. 2014, 48, 6726−6734.

(75) Yin, F.; John, G. F.; Hayworth, J. S.; Clement, T. P. Long-term monitoring data to describe the fate of polycyclic aromatic hydrocarbons in Deepwater Horizon oil submerged off Alabama's beaches. Sci. Total Environ. 2015, 508, 46−56.

(76) Nordvik, A. B. The technology windows-of-opportunity for marine oil spill response as related to oil weathering and operations. Spill Sci. Technol. Bull. 1995, 2, 17−46.

(77) Lewis, A. B.; Trudel, K.; Belore, R. C.; Mullin, J. V. Large-scale dispersant leaching and effectiveness experiments with oils on calm water. Mar. Pollut. Bull. 2010, 60, 244−254.

(78) McFarlin, K. M.; Prince, R. C.; Perkins, R.; Leigh, M. B. Biodegradation of dispersed oil in arctic seawater at −1 °C. PLoS One 2014, 9, e84297.

(79) Ourisson, G.; Albrecht, P. Hopanoids. 1. Geohopanoids: the most abundant natural products on Earth? Acc. Chem. Res. 1992, 25, 398−402.

(80) Valentine, D. L.; Fisher, G. B.; Bagby, S. C.; Nelson, R. K.; Reddy, C. M.; Sylva, S. P.; Woo, M. A. Fallout plume of submerged oil from Deepwater Horizon. Proc. Natl. Acad. Sci. U.S.A. 2014, 111, 15906−15911.

(81) Queimada, A. J.; Quinones-Cisneros, S. E.; Marrucho, I. M.; Coutinho, J. A. P.; Stenby, E. H. Viscosity and liquid density of asymmetric hydrocarbon mixtures. Int. J. Thermophys. 2003, 24, 1221−1239.

(82) Liu, K.; Wu, Y.; McHugh, M. A.; Baled, H.; Enick, R. M.; Morreale, B. D. Equation of state modeling of high-pressure, high-temperature hydrocarbon density data. J. Supercrit. Fluids 2010, 55, 701−711.

(83) Wakeham, W. A.; Cholakov, G. S.; Stateva, R. P. Liquid density and critical properties of hydrocarbons estimated from molecular structure. J. Chem. Eng. Data 2002, 47, 559−570.

(84) Alboudwarej, H.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W.; Akbarzadeh, K. Sensitivity of asphaltene properties to separation techniques. Energy Fuels 2002, 16, 462−469.

(85) Barrera, D. M.; Ortiz, D. P.; Yarranton, H. W. Molecular weight and density distributions of asphaltenes from crude oils. Energy Fuels 2013, 27, 2474−2487.

(86) Chanton, J.; Zhao, T.; Rosenheim, B. E.; Joye, S. B.; Bosman, S.; Brunner, C. A.; Yeager, K. M.; Diercks, A. R.; Hollander, D. Using natural abundance radiocarbon to trace the flux of petrocarbon to the seafloor following the Deepwater Horizon oil spill. Environ. Sci. Technol. 2014, 49, 847−854.

(87) Shiloach, J.; Fass, R. Growing E. coli to high cell density · a historical perspective on method development. Biotechnol. Adv. 2005, 23, 345−57.

(88) Levy, E. M.; Lee, K. Potential contribution of natural hydrocarbon seepage to benthic productivity and the fisheries of Atlantic Canada. Can. J. Fish. Aquat. Sci. 1988, 45, 349−352.

(89) Kostka, J. E.; Prakash, O.; Overholt, W. A.; Green, S. J.; Freyer, G.; Canion, A.; Delgardio, J.; Norton, N.; Hazen, T. C.; Huettel, M. Hydrocarbon-degrading bacteria and the bacterial community response in Gulf of Mexico beach sands impacted by the Deepwater Horizon oil spill. Appl. Environ. Microbiol. 2011, 77, 7962−7974.

(90) Dubinsky, E. A.; Conrad, M. E.; Chakraborty, R.; Bill, M.; Borglin, S. E.; Hollibaugh, J. T.; Mason, O. U.; Piceno, Y. M.; Reid, F. C.; Stringfellow, W. T.; Tom, L. M.; Hazen, T. C.; Andersen, G. L. Succession of hydrocarbon-degrading bacteria in the aftermath of the Deepwater Horizon oil spill in the Gulf of Mexico. Environ. Sci. Technol. 2013, 47, 10860−10867.

(91) Lamendella, R.; Strutt, S.; Borglin, S.; Chakraborty, R.; Tas, N.; Mason, O. U.; Hultman, J.; Prestat, E.; Hazen, T. C.; Jansson, J. K. Assessment of the Deepwater Horizon oil spill impact on Gulf coast microbial communities. Front. Microbiol. 2014, 5, 130.

(92) Rodriguez-R, L. M.; Overholt, W. A.; Hagan, C.; Huettel, M.; Kostka, J. E.; Konstantinidis, K. T. Microbial community successional patterns in beach sands impacted by the Deepwater Horizon oil spill. ISME J. 2015, DOI: 10.1038/ismej.2015.5.

(93) Uña, G. V.; García, M. J. N. Biodegradation of non-ionic dispersants in sea-water. Eur. J. Appl. Microbiol. Biotechnol. 1983, 18, 315−319.

(94) Cordon, T. C.; Maurer, E. W.; Stirton, A. J. The course of biodegradation of anionic detergents by analyses for carbon, methylene blue active substance and sulfate ion. J. Am. Oil Chem. Soc. 1970, 47, 203−206.

(95) Gray, J. L.; Kanagy, L. K.; Furlong, E. T.; Kanagy, C. J.; McCoy, J. W.; Mason, A.; Lauenstein, G. Presence of the Corexit component dioctyl sodium sulfosuccinate in Gulf of Mexico waters after the 2010 Deepwater Horizon oil spill. Chemosphere 2014, 95, 124−130.

(96) Kujawinski, E. B.; Kido Soule, M. C.; Valentine, D. L.; Boysen, A. K.; Longnecker, K.; Redmond, M. C. Fate of dispersants associated with the Deepwater Horizon oil spill. Environ. Sci. Technol. 2011, 45, 1298−1306.

(97) Hayworth, J. S.; Clement, T. P. Provenance of COREXIT-related chemical constituents found in nearshore and inland Gulf Coast waters. Mar. Pollut. Bull. 2012, 64, 2005−2014.

(98) White, H. K.; Lyons, S. L.; Harrison, S. J.; Findley, D. M.; Liu, Y.; Kujawinski, E. B. Long-term persistence of dispersants following the Deepwater Horizon oil spill. Environ. Sci. Technol. Lett. 2014, 1, 295−299.

(99) Roberts, J. R.; Reynolds, J. S.; Thompson, J. A.; Zaccone, E. J.; Shimko, M. J.; Goldsmith, W. T.; Jackson, M.; McKinney, W.; Frazer, D. G.; Kenyon, A.; Kashon, M. L.; Piedimonte, G.; Castranova, V.; Fedan, J. S. Pulmonary effects after acute inhalation of oil dispersant (COREXIT EC9500A) in rats. J. Toxicol. Environ. Health, Part A 2011, 74, 1381−1396.

(100) Krajnak, K.; Kan, H.; Waugh, S.; Miller, G. R.; Johnson, C.; Roberts, J. R.; Goldsmith, W. T.; Jackson, M.; McKinney, W.; Frazer, D.; Kashon, M. L.; Castranova, V. Acute effects of COREXIT EC9500A on cardiovascular functions in rats. J. Toxicol. Environ. Health, Part A 2011, 74, 1397−1404.

(101) Sriram, K.; Lin, G. X.; Jefferson, A. M.; Goldsmith, W. T.; Jackson, M.; McKinney, W.; Frazer, D. G.; Robinson, V. A.; Castranova, V. Neurotoxicity following acute inhalation exposure to the oil dispersant COREXIT EC9500A. J. Toxicol. Environ. Health, Part A 2011, 74, 1405−1418.

(102) Anderson, S. E.; Franko, J.; Lukomska, E.; Meade, B. J. Potential immunotoxicological health effects following exposure to COREXIT 9500A during cleanup of the Deepwater Horizon oil spill. J. Toxicol. Environ. Health, Part A 2011, 74, 1419−1430.

(103) Johansen, Ø.; Brandvik, P. J.; Farooq, U. Droplet breakup in subsea oil releases−Part 2: Predictions of droplet size distributions with and without injection of chemical dispersants. Mar. Pollut. Bull. 2013, 73, 327−335.

(104) Place, B. J.; Perkins, M. J.; Sinclair, E.; Barsamian, A. L.; Blakemore, P. R.; Field, J. A. Trace analysis of surfactants in Corexit oil dispersant formulations and seawater. Deep-Sea Res. 2014, DOI: 10.1016/j.dsr2.2014.01.015.

(105) Canevari, G. P. The effect of crude oil composition on dispersant performance. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1985; pp 441−444.

(106) Nedwed, T.; Canevari, G. P.; Clark, J. R.; Belore, R. New dispersant delivered as a gel. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 2005; pp 121−125.

(107) Finch, B. E.; Wooten, K. J.; Smith, P. N. Embryotoxicity of weathered crude oil from the Gulf of Mexico in mallard ducks (Anas platyrhynchos). Environ. Toxicol. Chem. 2011, 30, 1885−1891.

(108) Irie, K.; Kawaguchi, M.; Mizuno, K.; Song, J. Y.; Nakayama, K.; Kitamura, S. I.; Murakami, Y. Effect of heavy oil on the development of the nervous system of floating and sinking teleost eggs. Mar. Pollut. Bull. 2011, 63, 297−302.

(109) Almeda, R.; Baca, S.; Hyatt, C.; Buskey, E. J. Ingestion and sublethal effects of physically and chemically dispersed crude oil on marine planktonic copepods. Ecotoxicology 2014, 23, 988−1003.

(110) Garrett, R. M.; Pickering, I. J.; Haith, C. E.; Prince, R. C. Photooxidation of crude oils. Environ. Sci. Technol. 1998, 32, 3719−3723.

(111) Aeppli, C.; Carmichael, C. A.; Nelson, R. K.; Lemkau, K. L.; Graham, W. M.; Redmond, M. C.; Valentine, D. L.; Reddy, C. M. Oil weathering after the Deepwater Horizon disaster led to the formation of oxygenated residues. Environ. Sci. Technol. 2012, 46, 8799−8807.

(112) Goodman, R. Tar balls: the end state. Spill Sci. Technol. Bull. 2003, 8, 117−121.

(113) Barron, M. G.; Carls, M. G.; Short, J. W.; Rice, S. D.; Heintz, R. A.; Rau, M.; Di Giulio, R. Assessment of the phototoxicity of weathered Alaska North Slope crude oil to juvenile pink salmon. Chemosphere 2005, 60, 105−110.

(114) Payne, J. R.; Clayton, J. R.; McNabb, G. D.; Kirstein, B. E. Exxon Valdez oil weathering fate and behavior: model predictions and field observations 1. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1991, pp 641−654.

(115) Bobra, M. Water-in-oil emulsification: a physicochemical study. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1991; pp 483−488.

(116) Strøm-Kristiansen, T.; Lewis, A.; Daling, P. S.; Hokstad, J. N.; Singsaas, I. Weathering and dispersion of naphthenic, asphaltenic, and waxy crude oils. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1997; pp 631−636.

(117) Lessard, R. R.; DeMarco, G. The significance of oil spill dispersants. Spill Sci. Technol. Bull. 2000, 6, 59−68.

(118) Thingstad, T.; Pengerud, B. The formation of "chocolate mousse" from Statfjord crude oil and seawater. Mar. Pollut. Bull. 1983, 14, 214−216.

(119) Daling, P. S.; Leirvik, F.; Almås, I. K.; Brandvik, P. J.; Hansen, B. H.; Lewis, A.; Reed, M. Surface weathering and dispersibility of MC252 crude oil. Mar. Pollut. Bull. 2014, 87, 300−310.

(120) Gros, J.; Nabi, D.; Würz, B.; Wick, L. Y.; Brussaard, C. P. D.; Huisman, J.; van der Meer, J. R.; Reddy, C. M.; Arey, J. S. First day of an oil spill on the open sea: early mass transfers of hydrocarbons to air and water. Environ. Sci. Technol. 2014, 48, 9400−9411.

(121) Goldstein, B. D.; Osofsky, H. J.; Lichtveld, M. Y. The Gulf oil spill. N. Engl. J. Med. 2011, 364, 1334−1348.

(122) Atkinson, R.; Arey, J. Atmospheric degradation of volatile organic compounds. Chem. Rev. 2003, 103, 4605−4638.

(123) Deguillaume, L.; Leriche, M.; Amato, P.; Ariya, P. A.; Delort, A. M.; Pöschl, U.; Chaumerliac, N.; Bauer, H.; Flossmann, A. I.; Morris, C. E. Microbiology and atmospheric processes: chemical interactions of primary biological aerosols. Biogeosciences 2008, 5, 841−870.

(124) Colcomb, K.; Bedborough, D.; Lunel, T.; Swannell, R.; Wood, P.; Rusin, J.; Bailey, N.; Halliwell, C.; Davies, L.; Sommerville, M.; Dobie, A.; Mitchell, D.; McDonagh, M.; Lee, K.; Shimwell, S.; Davies, B.; Harries, D. Shoreline cleanup and waste disposal issues during the Sea Empress incident. In International Oil Spill Conference Proceedings; American Petroleum Institute: Washington, DC, 1997; pp 195−198.

(125) Michel, J.; Owens, E. H.; Zengel, S.; Graham, A.; Nixon, Z.; Allard, T.; Holton, W.; Reimer, P. D.; Lamarche, A.; White, M.; Rutherford, N.; Childs, C.; Mauseth, G.; Challenger, G.; Taylor, E. Extent and degree of shoreline oiling: Deepwater Horizon oil spill, Gulf of Mexico, USA. PLoS One 2013, 8, e65087.

(126) Wang, Z.; Fingas, M.; Owens, E. H.; Sigouin, L.; Brown, C. E. Long-term fate and persistence of the spilled Metula oil in a marine salt marsh environment: degradation of petroleum biomarkers. J. Chromatogr. A 2001, 926, 275−290.

(127) Owens, E. H.; Taylor, E.; Humphrey, B. The persistence and character of stranded oil on coarse-sediment beaches. Mar. Pollut. Bull. 2008, 56, 14−26.

(128) Defeo, O.; McLachlan, A.; Schoeman, D. S.; Schlacher, T. A.; Dugan, J.; Jones, A.; Lastra, M.; Scapini, F. Threats to sandy beach ecosystems: a review. Estuarine, Coastal Shelf Sci.. 2009, 81, 1−12.

(129) Burns, K. A.; Garrity, S. D.; Levings, S. C. How many years until mangrove ecosystems recover from catastrophic oil spills? Mar. Pollut. Bull. 1993, 6, 239−248.

(130) Mendelssohn, I. A.; Andersen, G. L.; Baltz, D. M.; Caffey, R. H.; Carman, K. R.; Fleeger, J. W.; Joye, S. B.; Lin, Q.; Maltby, E.; Overton, E. B.; Rozas, L. P. Oil impacts on coastal wetlands: implications for the Mississippi River Delta ecosystem after the Deepwater Horizon oil spill. BioScience 2012, 62, 562−574.

(131) Michel, J.; Rutherford, N. Impacts, recovery rates, and treatment options for spilled oil in marshes. Mar. Pollut. Bull. 2014, 82, 19−25.

(132) Bernabeu, A. M.; Nuez de la Fuente, M.; Rey, D.; Rubio, B.; Vilas, F.; Medina, R.; González, M. E. Beach morphodynamics forcements in oiled shorelines: coupled physical and chemical processes during and after fuel burial. Mar. Pollut. Bull. 2006, 52, 1156−1168.

(133) Pineda-Flores, G.; Boll-Argüello, G.; Lira-Galeana, C.; Mesta-Howard, A. M. A microbial consortium isolated from a crude oil sample that uses asphaltenes as a carbon and energy source. Biodegradation 2004, 15, 145−151.

(134) Tavassoli, T.; Mousavi, S. M.; Shojaosadati, S. A.; Salehizadeh, H. Asphaltene biodegradation using microorganisms isolated from oil samples. Fuel 2012, 93, 142−148.

(135) Hayes, M. H. B. Solvent systems for the isolation of organic components from soils. Soil Sci. Soc. Am. J. 2006, 70, 986−994.

(136) Michaels, D.; Howard, J. Review of the OSHA-NIOSH response to the Deepwater Horizon oil spill: protecting the health and safety of cleanup workers. PLoS Curr. 2012, 4, e4fa83b7576b6e.

(137) Schwarz, J. R.; Walker, J. D.; Colwell, R. R. Deep-sea bacteria: growth and utilization of hydrocarbons at ambient and in situ pressure. Appl. Microbiol. 1974, 28, 982−986.

(138) Kimes, N. E.; Callaghan, A. V.; Aktas, D. F.; Smith, W. L.; Sunner, J.; Golding, B. T.; Drozdowska, M.; Hazen, T. C.; Suflita, J. M.; Morris, P. J. Metagenomic analysis and metabolite profiling of deep-sea sediments from the Gulf of Mexico following the Deepwater Horizon oil spill. Front. Microbiol. 2013, 4, 50.

(139) Van Hamme, J. D.; Ward, O. P. Influence of chemical surfactants on the biodegradation of crude oil by a mixed bacterial culture. Can. J. Microbiol. 1999, 45, 130−137.

(140) Lindstrom, J. E.; Braddock, J. F. Biodegradation of petroleum hydrocarbons at low temperature in the presence of the dispersant COREXIT 9500. Mar. Pollut. Bull. 2002, 44, 739−747.

(141) Venosa, A. D.; Holder, E. L. Biodegradability of dispersed crude oil at two different temperatures. Mar. Pollut. Bull. 2007, 54, 545−553.

(142) Hamdan, L. J.; Fulmer, P. A. Effects of COREXIT® EC9500A on bacteria from a beach oiled by the Deepwater Horizon spill. Aquat. Microb. Ecol. 2011, 63, 101−109.

(143) Urbanczyk, H.; Ast, J. C.; Higgins, M. J.; Carson, J.; Dunlap, P. V. Reclassification of Vibrio fischeri, Vibrio logei, Vibrio salmonicida and Vibrio wodanis as Aliivibrio fischeri gen. nov., comb. nov., Aliivibrio logei comb. nov., Aliivibrio salmonicida comb. nov. and Aliivibrio wodanis comb. nov. Int. J. Syst. Evol. Microbiol. 2007, 57, 2823−2829.

(144) Fuller, C.; Bonner, J.; Page, C.; Ernest, A.; McDonald, T.; McDonald, S. Comparative toxicity of oil, dispersant, and oil plus dispersant to several marine species. Environ. Toxicol. Chem. 2004, 23, 2941−2949.

(145) McManus, M. A.; Woodson, C. B. Plankton distribution and ocean dispersal. J. Exp. Biol. 2015, 215, 1008−1016.

(146) Prairie, J. C.; Sutherland, K. R.; Nickols, K. J.; Kaltenberg, A. M. Biophysical interactions in the plankton: a cross-scale review. Limnol. Oceanogr. 2012, 2, 121−145.

(147) Ottesen, E. A.; Young, C. R.; Eppley, J. M.; Ryan, J. P.; Chavez, F. P.; Scholin, C. A.; DeLong, E. F. Pattern and synchrony of gene expression among sympatric marine microbial populations. Proc. Natl. Acad. Sci. U.S.A. 2013, 110, E488−E497.

(148) Dispersant Tools, Job Aids and Decision Process; Region X Regional Response Team, 2015. www.rrt10nwac.com/Files/NWACP/2015/Section%209406.pdf.

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Peter Egan[peter.egan@total.com]
From: Malcolm Gore
Sent: Mon 4/25/2016 2:57:21 PM
Subject: Finasol OSR 52 Sample Request

Hello Robin
I am writing with respect to your email below regarding a sample request of Total Finasol OSR 52.
Clear Coast is the custodian of the product stored here in Houston for Total.
I will arrange the sample as requested.
Please confirm the following:

Contact:
Robyn Conmy 513-569-7090 (office)

Deliver to:

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

Quantity:

2 US Gallons.

On receipt of confirmation I will get the samples drawn, packaged and dispatched.
Regards

Malcolm

Malcolm Gore
President

CLEAR COAST

+1 832 244 1533
malcolm.gore@clearcoastllc.com
www.clearcoastllc.com

From: Conmy, Robyn
Sent: Monday, April 18, 2016 10:47 AM
To: 'peter.egan@total.com' <peter.egan@total.com>
Cc: Wilson, Gregory <Wilson.Gregory@epa.gov>; Principe, Vanessa
<Principe.Vanessa@epa.gov>

Subject: purchase of Finasol OSR52

Mr. Egan,

This follows up our telephone conversation of April 11.

As discussed, EPA is seeking to acquire a number of dispersant products listed on the NCP Subpart J Product Schedule for the purposes of both toxicity and efficacy testing. The product testing is intended to further inform currently proposed regulatory actions under Subpart J of the National Contingency Plan. The products will in addition be used to support our general research in the area of oil spill response.

Your product Finasol OSR52 has been identified as one of interest, as it is commonly stockpiled in the U.S. Not only could the product be encountered when presented with a response situation, but including this dispersant product in toxicity and efficacy testing studies will also allow for comparison and consistency with other existing and ongoing studies by EPA and other federal agencies. EPA's Office of Research and Development (ORD) will be conducting the dispersant studies.

At this time we are seeking 2 U.S. gallons of the product.

We appreciate your time and attention to this request.

Respectfully,

Robyn Conmy

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]; Devi Sundaravadivelu[devis.255@gmail.com]
From: Holder, Edith
Sent: Wed 4/20/2016 7:28:58 PM
Subject: RE: dates?

Devi and I picked 10-11:30 AM. I have reserved a room.

Notes from our discussion:

Burn study: You are going to talk with Brian to ascertain what he needs from us.

I will talk again with Raghu to find out about purge and trap instrument for measuring BTEX of pads and raw oil

I don't understand how he jumped from amount measured on the pad to the total oil budget

Tensiometer: Devi will get a quote for an outside lab to make some measurements.

Explore purchase of instrument, decide what specs we need, how long it would take Pegasus to make a purchase?

Dispersants: acquisition thru OEM slow, have 600 + ml of Accel, Finasol, and Dispersit, but not of Corexit

SWA will schedule group meeting next week

Begin discussion on research plans for next year

Edie

From: Conmy, Robyn
Sent: Wednesday, April 20, 2016 2:55 PM
To: Holder, Edith <holder.edith@epa.gov>; Devi Sundaravadivelu <devis.255@gmail.com>
Subject: dates?

I'm available all next Wednesday for SWA discussion.

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

To: chris.barker@noaa.gov[chris.barker@noaa.gov]; CJ.Beegle-Krause@sintef.no[CJ.Beegle-Krause@sintef.no]; Conmy, Robyn[Conmy.Robyn@epa.gov]; thomas.s.coolbaugh@exxonmobil.com[thomas.s.coolbaugh@exxonmobil.com]; fingasmerv@shaw.ca[fingasmerv@shaw.ca]; ali.khelifa@ec.gc.ca[ali.khelifa@ec.gc.ca]; jrpayne@sbcglobal.net[jrpayne@sbcglobal.net]; wspegau@pwssc.org[wspegau@pwssc.org]; creddy@whoi.edu[creddy@whoi.edu]
Cc: nancy.kinner@unh.edu[nancy.kinner@unh.edu]
From: Mandsager, Kathy
Sent: Tue 4/19/2016 3:48:12 PM
Subject: State-of-Science for Dispersants: Physical Transport & Chemical Behavior
COMBINED_Physical Transport and Chemical Behavior PUBLIC INPUT.docx

Dear scientific panel:

The public input period has closed on the *Physical Transport & Chemical Behavior* document. We received 10 individual responses. A collated list of these responses are attached for your perusal.

It is now time to schedule another WebEx meeting in order to discuss this information and/or incorporate or edit the original document as you deem appropriate. Please use the doodle poll to select a time for this WebEx meeting in May. It is time-zone enabled for your convenience and if you could **respond by Monday 4/25** it will help in securing a date and getting it on your busy calendars.

Here is the doodle poll>> http://doodle.com/poll/8wn9ez5xpmeyhw2p

Thank you so much!

Kathy Mandsager

Coastal Response Research Center

Center for Spills and Environmental Hazards

220 Gregg Hall, 35 Colovos Rd

University of New Hampshire

Durham, NH 03824

603.862.1545

To: Musson, Steve[Musson.Steve@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]; Venkatapathy, Raghuraman[Venkatapathy.Raghuraman@epa.gov]; Schubauer-Berigan, Joseph[Schubauer-Berigan.Joseph@epa.gov]; Meghan Welch[meghan.welch@ptsied.com]
From: Holder, Edith
Sent: Tue 5/19/2015 8:02:24 PM
Subject: RE: HASP Annual Review Due
Finasol.pdf
oil spill SDS.pdf

Here are the records in our lab.

Biodispers and Dispersit SPC 1000 are old dispersants in our lab and are lines 11 and 12 of last year's HASP. The MSDS are not in my current notebook as we are not currently using them, but we will look for them in boxes of old records.

FFT Solution was just received in our lab, and we will follow up with the manufacturer for the SDS.

The SDS has been requested from the manufacturer of EPA Oil Field Solution, but we have not received it. An additional contact will be made.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Musson, Steve
Sent: Tuesday, May 19, 2015 10:41 AM
To: Holder, Edith
Cc: Conmy, Robyn; Venkatapathy, Raghuraman; Schubauer-Berigan, Joseph
Subject: RE: HASP Annual Review Due

Hi Edie,

There were many new dispersants. I appreciate you taking the time to add them to the HASP. I want to stress that the lab is not allowed to receive any new chemicals until the HASP is revised before they are received. Otherwise EPA and Pegasus are not meeting OSHA regulations for Hazcom.

I tried to find as many MSDS/SDS online that I could for the dispersants/SWAs. But I have highlighted several that we do not have a MSDS/SDS on file and I could not find online. Please provide a copy of those. Once we get those we will be able to route the HASP. Until then, no work is allowed using these highlighted items.

Steve

From: Holder, Edith
Sent: Thursday, May 14, 2015 2:36 PM
To: Musson, Steve
Cc: Conmy, Robyn
Subject: RE: HASP Annual Review Due

Steve,

Enclosed is a revised HASP. During the last year we have received more oils, dispersants, and SWA. Those products have been added in tables by category at the end of the chemical list. There are no other changes.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Musson, Steve
Sent: Wednesday, May 13, 2015 10:09 AM
To: DelaCruz, Armah; Nadagouda, Mallikarjuna; Schaefer, Frank; Silvestri, Erin; Pressman, Jonathan; Wahman, David; Feldhake, David; quintero.maria@azdeq.gov; Shanks, Orin; Kelty, Catherine; Shoemaker, Jody; Varma, Rajender; Donohue, Maura; Pfaller, Stacy; Jewett, David; Hargrove, Kristie; Al-Abed, Souhail; Pinto, Patricio; Brooks, Michael; Wood, Lynn; Conmy, Robyn; Holder, Edith; Zaffiro, Alan; Batt, Angela; See, Mary Jean
Subject: HASP Annual Review Due

Everyone,

You are getting this email because your HASP is due for its annual review in May or June.

One of the staff listed below for each HASP, please take a moment to review the HASP and respond to this email by either:

1. State "The HASP is current and no changes need to be made"

2. State "The HASP is no longer necessary, please inactivate it"

3. Send the HASP back to me with any changes that need to be made to revise it.

Thanks,

Steve

Stephen Musson, PhD, CIH, CHMM

Safety, Health, and Environmental Management Program Manager

US EPA National Risk Management Research Laboratory

26 W. Martin Luther King Drive

Cincinnati OH 45268

513-569-7969

Division	HASP #	Rev #	Title	Date Review Due	Principal Investigator #1	Principal Investigator #2	Principal Investigator #3	Prepared	Branch	Expir Date
MCE	2017-087	R1	Cyanobacteria and their Cyanotoxins	6/16/2016	de la Cruz,			de la Cruz,	MiERB	R31

					Armah A.			Armah A.		
WSW	ORD	4 030	Sulfate and Phosphate Removal using novel synthesized media	6/17/20..	Mohan, Gayathri Ram	Nadagouda,Mall...		Mohan, Gayathri Ram	IO	3/31/
TCA	2013 2 033		Optimization of Bacillus anthracis Spore Recovery from Soil	6/18/20..	Schaefer, Frank...	Silvestri, Erin		Feldhake, David	None Chosen	4/30/
WSW	ORD 2 045		Chloraminated Drinking Water Distribution System Nitrification	5/15/20..	Pressman, Jonathan	Wahman,David		Quinter, Kalya	TTE	6/30/
WSW	ORD 9 047		Genome Fragment Enrichment	6/30/20..	Shanks,Orin			Kelty, Catherine	MC	6/30/
MCE	ORD 9 062		Measuring Sucralose In Recreational Waters To Identify Human-Based Fecal Pollution: A Pilot Study	6/15/20..	Shoemaker,Jody			Shoemaker,Jody	CER	3/31/
STD	2014 0 003		Highly Selective Photosynthesis Processes over Visible-Light-Induced Micro- and Nano-structured Photocatalysts	5/29/20..	Baig,Nasir	Varma,Rajender		Baig,Nasir	GPB	1/31/
MCE	ORD 9 014		General Laboratory Practices Associated with Proteomic Research	5/30/20..	Donohue,Maura	Pfaller,Stacy		Donohue,Maura	NER	3/31/
GWE	ORD 9 023		Laboratory 4	5/30/20..	Jewett,David			Hargrove,Kristie	ARR	8/30/
LRP	2014 1 024		Metal Migration from Drinking Water Treatment Plant (DWTP) Sludges and Landfill Soils under Different Redox Conditions	6/4/2015	Al-Abed,Souhail			Pinto,Patricia	WM	4/30/
GWE	ORD 9 032		Predicting DNAPL Source Zone and Plume Response Using Site Measured Characteristics	6/30/20..	Brooks,Michael	Wood,Lynn		Wood,Lynn	SR	6/30/
LRP	2014 0 033		Oil Spill Research Including Work with Dispersants, Surface Washing Agents (SWAs), and Oil Degrading Microbes	6/30/20..	Conmy,Robyn			Holder,Edith	LSM	6/30/
SRM	2014 0 039		Second Laboratory Demonstration for Microcystins in Drinking Water using Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry	6/30/20..	Adams,William			Zaffiro,Alan	TSC	6/30/
EER	2014 0 016		Aquatic Studies Analytical Support using Solid Phase Extraction and Gas Chromatography/Mass	6/30/20..	Batt,Angela			See,Mary Jean	MIR	6/30/

		Spectrometry							

To: Holder, Edith[holder.edith@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]; Venkatapathy,
Raghuraman[Venkatapathy.Raghuraman@epa.gov]; Schubauer-Berigan, Joseph[Schubauer-
Berigan.Joseph@epa.gov]
From: Musson, Steve
Sent: Tue 5/19/2015 2:40:30 PM
Subject: RE: HASP Annual Review Due
2014-033 Rev 1 SHEM Comments.docx

Hi Edie,

There were many new dispersants. I appreciate you taking the time to add them to the HASP. I want to stress that the lab is not allowed to receive any new chemicals until the HASP is revised before they are received. Otherwise EPA and Pegasus are not meeting OSHA regulations for Hazcom.

I tried to find as many MSDS/SDS online that I could for the dispersants/SWAs. But I have highlighted several that we do not have a MSDS/SDS on file and I could not find online. Please provide a copy of those. Once we get those we will be able to route the HASP. Until then, no work is allowed using these highlighted items.

Steve

From: Holder, Edith
Sent: Thursday, May 14, 2015 2:36 PM
To: Musson, Steve
Cc: Conmy, Robyn
Subject: RE: HASP Annual Review Due

Steve,

Enclosed is a revised HASP. During the last year we have received more oils, dispersants, and SWA. Those products have been added in tables by category at the end of the chemical list. There are no other changes.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Musson, Steve
Sent: Wednesday, May 13, 2015 10:09 AM
To: DelaCruz, Armah; Nadagouda, Mallikarjuna; Schaefer, Frank; Silvestri, Erin; Pressman, Jonathan; Wahman, David; Feldhake, David; quintero.maria@azdeq.gov; Shanks, Orin; Kelty, Catherine; Shoemaker, Jody; Varma, Rajender; Donohue, Maura; Pfaller, Stacy; Jewett, David; Hargrove, Kristie; Al-Abed, Souhail; Pinto, Patricio; Brooks, Michael; Wood, Lynn; Conmy, Robyn; Holder, Edith; Zaffiro, Alan; Batt, Angela; See, Mary Jean
Subject: HASP Annual Review Due

Everyone,

You are getting this email because your HASP is due for its annual review in May or June.

One of the staff listed below for each HASP, please take a moment to review the HASP and respond to this email by either:

1. State "The HASP is current and no changes need to be made"

2. State "The HASP is no longer necessary, please inactivate it"

3. Send the HASP back to me with any changes that need to be made to revise it.

Thanks,

Steve

Stephen Musson, PhD, CIH, CHMM

Safety, Health, and Environmental Management Program Manager

US EPA National Risk Management Research Laboratory

26 W. Martin Luther King Drive

Cincinnati OH 45268

513-569-7969

Division	HASP #	Rev #	Title	Date Review Due	Principal Investigator #1	Principal Investigator #2	Principal Investigator #3	Preparer	Branch	Expiration Date
MCEB	2021 087		Cyanobacteria and their Cyanotoxins	6/16/20	de la Cruz, Armah A.			de la Cruz, Armah A.	MiE	R33 1
WSWR	2013 030		Sulfate and Phosphate Removal using novel synthesized media	6/17/20	Mohan, Gayathri	Nadagouda,Mall		Mohan, Gayathri	IO	3/31/

					Ram			Ram		
TCA	2013	033	Optimization of Bacillus anthracis Spore Recovery from Soil	6/18/2013	Schaefer, Frank	Shastri, Erin		Feldhake, David	None Chosen	4/30/
WSWRD	2012	045	Chloraminated Drinking Water Distribution System Nitrification	5/15/2012	Pressman, Jonathan	Wahman, David		Quinter, Kalya	TTEB	6/30/
WSWRD	2013	047	Genome Fragment Enrichment	6/30/2013	Shanks, Orin			Kelty, Catherine	MCB	6/30/
MCEARD	2010	062	Measuring Sucralose In Recreational Waters To Identify Human-Based Fecal Pollution: A Pilot Study	6/15/2010	Shoemaker, Jody			Shoemaker, Jody	CERB	1/
STD	2014	003	Highly Selective Photosynthesis Processes over Visible-Light-Induced Micro- and Nano-structured Photocatalysts	5/29/2014	Baig, Nasir	Sharma, Rajender		Baig, Nasir	GPB	1/31/
MCEARD	2014	014	General Laboratory Practices Associated with Proteomic Research	5/30/2014	Donohue, Maura	Pfaller, Stacy		Donohue, Maura	NERL	1/
GWERD	2014	023	Laboratory 4	5/30/2014	Jewett, David			Hargrove, Kristie	ARB	6/30/
LRPCD	2014	024	Metal Migration from Drinking Water Treatment Plant (DWTP) Sludges and Landfill Soils under Different Redox Conditions	6/4/2014	Al-Abed, Souhail			Pinto, Patricio	WMD	6/30/
GWERD	2014	032	Predicting DNAPL Source Zone and Plume Response Using Site Measured Characteristics	6/30/2014	Brooks, Michael Lynn			Wood, Lynn	SRB	6/30/
LRPCD	2014	033	Oil Spill Research Including Work with Dispersants, Surface Washing Agents (SWAs), and Oil Degrading Microbes	6/30/2014	Conmy, Robyn			Holder, Ed	ESMD	6/30/
SRMRD	2014	039	Second Laboratory Demonstration for Microcystins in Drinking Water using Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry	6/30/2014	Adams, William			Zaffiro, Alan	TSC	6/30/
EERD	2014	016	Aquatic Studies Analytical Support using Solid Phase Extraction and Gas Chromatography/Mass Spectrometry	6/30/2014	Batt, Angela			See, Mary Jean	MIRB	6/30/

Health and Safety Plan

Title: Oil Spill Research Including Work with Dispersants, Surface Washing Agents (SWAs), and Oil Degrading Microbes
Principal Investigator(s):   Robyn Conmy, Edith Holder
Office: ORD
Laboratory:
    NRMRL Division:
    LRPCD Branch:
    ESMB
Building: AWBERC
Room/Lab #:   703, 701, 708, Constant Temperature Room 710

Approvals

I have read and approve the attached Health and Safety Plan in conformance with the ORD Facility Chemical Hygiene Plan and Health & Safety Plan Policy.   I certify that the workplace hazards, routinely and non-routinely encountered by employees, during the described activities, and for which Personal Protective Equipment has been provided, have been assessed for the determination of Personal Protective Equipment required, in compliance with 29 CFR 1910 Subpart I.

Name	Phone	Signature	Date
Edith Holder PREPARER	569-7178		
Dr. Robyn Conmy PRINCIPAL INVESTIGATOR	569-7090		
Dr. Joseph Schubauer-Berigan IMMEDIATE SUPERVISOR	569-7734		
Dr. Raghu Venkatapathy PTSI On-Site Manager	569-7077		
(Additional Approvals: such as CO-PI or Contractor Manager)			
Steve Musson	569-7969		

CHEMICAL HYGIENE OFFICER

Additional information on the completion of a Health & Safety Plan may be found at the SHEM Intranet Site.

Laboratory / Field Staff Concurrence

I have read, understood and will comply with all the requirements of the attached Health and Safety Plan, SDS's, and the rules contained in the U. S. EPA- Facilities Chemical Hygiene Plan. I have also had the opportunity to ask any questions, and had my questions satisfactorily answered prior to my beginning work under this plan.

Name (Print)	Employer (EPA, ORISE, Contractor name, etc.)	Lab (L), Field (F), or Both?	Signature	Date

Project Description

Background:

Unintentional releases of oil into coastal waters may result in oil becoming stranded on shorelines. Oil that reaches the shoreline can have a severe effect on the local environment, including toxic exposures and smothering of biota in direct contact with the oil. Surface washing agents (SWAs) are chemical agents intended to enhance the removal of oil from shoreline surfaces, thereby minimizing detrimental effects to impacted biota. Dispersants are chemical agents intended to break up the oil by reducing the oil-water interfacial surface tension, which will eventually promote dispersion of oil droplets into the water column. It is necessary to evaluate the potential benefits as a remediation aide of these two classes of compounds as well as the long term ramifications to the environment of their use.

Indigenous bacteria have the capability of removing oil components by biodegradation. The capability of populations from different sources to biodegrade different oils as well as the interactions of microbial populations to the various dispersants and SWAs is a subject for current study.

Laboratory Activities

This laboratory has done previous studies looking at the effects of dispersants, SWA, bioremediation products, and microbes enriched from sediments and water. From an earlier QAAP 386-Q11-0, endorsed 7 June 2002: "The U.S. Environmental Protection Agency's (EPA) Oil Spill Research Program encompasses several major objectives: 1) to develop and/or conduct scientifically sound and defensible protocols for testing the effectiveness of commercial bioremediation products on crude and refined oil in various environments, 2) to develop and/or conduct chemical and microbiological methods for characterizing changes in the chemical and biological composition of oil-contaminated matrices, such as beach material, soil, or water; and 3) to conduct research defining the proper conditions needed to bring about oil spill cleanup in the field. Research to address these objectives was initiated under Quality Assurance Project Plan (QAPP)ID No. C-781-B. The work performed earlier used Alaskan oil and Alaskan cultures. The current research will include Gulf of Mexico oil and cultures, as well as other oils of interest such as Dilbit and freshwater cultures from the Enbridge spill in Kalamazoo, MI. If new spills occur, oil and sediments from the impacted site may come under investigation.

Analysis of oil in water will be measured by Fluorometry. Samples of oil that have been extracted into either methylene chloride or hexane will be measured using UV/Vis Spectrophotometry or GC/MS. The current work will use the methods listed in the following QAPPs and HASPS which can be found on the L drive under L:Public\NRMRL-PUB\Holder\OilSpill\HASP&QAPP:

\QAPP 490-Q5-0.doc Development of a Surface Washing Agent Testing Protocol endorsed October 2004 Amendment to QAPP 490-Q5-0 submitted November 2009, resubmitted to WAM July 2010 and to QA September 2010

\Natural Substrate SOP.doc The Natural Substrate Protocol for Determining Effectiveness of Surface Washing Agents

\SOP UV vis.doc Analysis of Oil Concentration in DCM by UV/VIS Spectrophotometry

\FDOM analysis.doc Standard Operating Protocol for Fluorescent Dissolved Organic Matter (FDOM)

In subdirectory QAPP 2013:
QAPP L-14866-QP-1-6 Development and Revision of Procedures for the Code of Federal Regulations (CFR)
    Appendix C to Part 300, Oil Spill Product Testing Protocols

    Appendix A: Oil Dispersant Testing, Standard Operating Procedure for Determining Effectiveness of Oil

Dispersants Using the Baffled Flask Test, May 2013

Appendix B: Bioremediation Product Testing, Standard Operating Procedure for the Bioremediation Agent Effectiveness Test Protocol, May 2013

Appendix C: Oil Analysis SOPs, GC/MS procedures, May 2013
    SOP 1: Glassware Cleaning Procedure for Oil Spill Projects
    SOP 2: Preparation of Surrogate Recovery Standards
    SOP 3: Preparation of Internal Standard Solution
    SOP 4: Preparation of Working Standards, Check Standards, and Oil Standards for GC/MS Consistency.
    SOP 5: GC/MS Method for the Analysis of Crude Oil Samples

A QAPP for specific research utilizing fluorescence spectrometry will be developed when this research is initiated.

A majority of the analytical methods are common to multiple projects and activities conducted within the oil spill program. The analytical work covered under this HASP include experiments with oil dispersants, surface washing agents (SWA), and oil degrading bacteria enriched from natural sources. Abiotic testing of the dispersants and SWA testing will utilize different oils and different products, varying parameters of application, temperature, weathering effects, and substrate. Biotic experiments will include biodegradation studies using a sacrificial shake flask experimental design.

The instruments that will be used for measuring oil components are a Shimadzu UV 1800 Spectrophotometer, Horiba Fluorolog3 Spectrofluorometer, WetLabs, Inc. ECO Submersible Fluorometer, and Agilent 6890 Gas Chromatograph with a 5973 Mass Spectrometer Detector. For all experiments, solvent (water, dichloromethane (DCM) or hexane) extracts of oil will be produced for analytical measurement.

Room 703 is the base lab for the various activities. The GC/MS will be located in room 708. CTR 710 will be used for 5oC work and 708 for work at 25oC. Storage of oil is in 703, storage of frozen samples is in 701, and storage of refrigerated samples is in 701 and CTR 710.

The full notice regarding dichloromethane (DCM) is given at the end of this document.

Physical Hazards Summary
The physical hazards marked below have been identified as present during the performance of the project. Job hazards for specific steps are described in the Job Hazard Analysis Table at the end of the HASP. The RSO shall be included in the list of reviewers/approval for all plans incorporating radioactive materials, radioactive devices, or radiation sources. **"L" is for Laboratory Activities; "F" is for Field Activities.**

Physical Hazards		Physical Hazards	
Electrical Hazards		Noise	
Radioactive Materials		Temperature	L
Non-Ionizing Radiation		Illumination	
Ionizing Radiation		Compressed Gas	L
Heavy Lifting		Sharp Objects / Tools	
Vibration		Slips, Trips, Falls	
UV light/radiation			
Other (Specify) Rotating Equipment (Laboratory Shaker)			L

PPE Summary

The PPE items marked below are required to be utilized during performance of the project.
PPE requirements for specific steps are described in the Job Hazard Analysis Table at the end of
*the HASP. **"L" is for Laboratory Activities; "F" is for Field Activities.***

Face / Eye Protection	
Safety Glasses w/ Side Shields	L
Chemical Splash Goggles	L
Face Shield	L
Other (specify)	
Ear Protection	
Ear Plugs (Foam Inserts)	
Both Ear Plugs and Ear Muffs	
Ear Muffs	
Other (specify)	
Hand Protection	
Chemical – Nitrile disposable exam	L
Chemical - Latex disposable exam	
Chemical – Butyl disposable exam	
Chemical - Silver Shield®	L
Chemical – Ansel Barrier®	
Cotton	
Leather	
Cut Resistant (Kevlar ®)	
Other (specify) – thermal protective	L
Other (specify) – Polypropylene Gloves (see FDOM SOP)	L
Protective Clothing	
Lab Coat	L
Lab Apron	
Jumpsuit	
Shoe covers	
Oversleeves	
Other (specify)	

Equipment Requirements

The safety equipment/engineering controls marked below(X) are required to be utilized during performance of the project. Requirements for specific steps are described in the Job Hazard Analysis Table at the end of the HASP.

Chemical Fume Hood	x
Biological Safety Cabinet	
Walk-in / Bulking Hood	
Radiological Fume Hood	
Balance Enclosure	
Clear Air Bench (laminar flow hood)	
Spot Ventilation Unit (Snorkel)	
Local Exhaust Ventilation	
Canopy Hood	

Liquid Scintillation Counter	
Refrigerator / Freezer	x
Deep Freezer	x
Other (specify) – spectrophotometer / shaker / GC/MS/ drying oven and muffle furnace	x

Chemicals to be Used

EPA utilizes an online service, Chemwatch, to provide Safety Data Sheets (SDS) to employees.
http://jr.chemwatch.net/chemwatch.web
Account: epa   User Name: Everyone Password: 120270.

If the SDS is not available through Chemwatch, a hardcopy of the manufacturer supplied SDS must be submitted to the SHEM office for upload to the Chemwatch system. . __ALL fields must be completed in the table below for all chemicals used in the project.__

Item #	Chemical Name	CAS#	Project Use	Disposal Method for Unused Chemicals	Notes
			Ex. Reagent, Standard, or Specific task #	S = Sink T = Trash W = Chemical Waste Program	(EPA waste codes, special hazards, ingredients, etc.)
1	Dichloromethane	75-09-2	Solvent	W	C
2	Hexane	110-54-3	Solvent	W	C
3	Petroleum Crude Oil	8002-05-9	Reagent	W	H
4	Biodispers		Dispersant	W	H
5	NEOS AB3000		Dispersant	W	H
6	Sodium Sulfate	7757-82-6	Reagent	W	C
7	Sea Salts (Sigma) (or Instant Ocean)	Mixture	Media	S or T	C
8	Bushnell-Haas Broth		Media	S or T	N/A
9	Sodium Chloride	7647-14-5	Media	S	C
10	Potassium Chloride	7447-40-7	Media	S	C
11	Potassium Bromide	7758-02-3	Media	W	C
12	Sodium Borate	1303-96-4	Media	S	C
13	Magnesium Chloride	7791-18-6	Media	S or T	C
14	Calcium Chloride	10043-52-4	Media	S or T	C
15	Strontium Chloride	10476-85-4	Media	W	C
16	Sodium Bicarbonate	7757-82-6	Media	S or T	C
17	Potassium Nitrate	7757-79-1	Media	W	C
18	Iron Chloride	10025-77-1	Media	W	C
19	Sodium Tripolyphosphate	7722-88-5	Media	W	C
20	Sodium Hydroxide	1310-73-2	reagent	Neutralize 6 < pH < 9	C
21	Hydrochloric Acid	7647-01-0	Reagent, acid washing, fluorometry	Neutralize 6 < pH < 9	C
22	Acenaphthene	00083-32-9	standard	W	C

23	Acenaphthylene	00208-96-8	standard	W	C
24	Benzo(a)anthracene	00056-55-3	standard	W	C
25	Biphenyl	00092-52-4	standard	W	C
26	2,6-Dimethylnaphthalene	00581-42-0	standard	W	C
27	3,6-Dimethylphenanthrene	01576-67-6	standard	W	C
28	1-Methylnaphthalene	00090-12-0	standard	W	C
29	2-Methylphenanthrene	02531-84-2	standard	W	C
30	2,3,5-Trimethylnaphthalene	02245-38-7	standard	W	C
31	Decane	00124-18-5	standard	W	C
32	Undecane	01120-21-4	standard	W	C
33	Dodecane	00112-40-3	standard	W	C
34	Tridecane	00629-50-5	standard	W	C
35	Tetradecane	00629-59-4	standard	W	C
36	Pentadecane	00629-62-9	standard	W	C
37	Hexadecane	00544-76-3	standard	W	C
38	Heptadecane	00629-78-7	standard	W	C
39	Octadecane	00593-45-3	standard	W	C
40	Nonadecane	00629-92-5	standard	W	C
41	Eicosane	00112-95-8	standard	W	C
42	Heneicosane	00629-94-7	standard	W	C
43	Docosane	00629-97-0	standard	W	C
44	Tricosane	00638-67-5	standard	W	C
45	Tetracosane	00646-31-1	standard	W	C
46	Pentacosane	00629-99-2	standard	W	C
47	Hexacosane	00630-01-3	standard	W	C
48	n-Heptacosane	00593-49-7	standard	W	C
49	Octacosane	00630-02-4	standard	W	C
50	n-Nonacosane	00630-03-5	standard	W	C
51	n-Triacontane	00638-68-6	standard	W	C
52	n-Hentriacontane	00630-04-6	standard	W	C
53	n-Dotriacontane	00544-85-4	standard	W	C
54	n-Tritriacontane	00630-05-7	standard	W	C
55	n-Tetratriacontane	14167-59-0	standard	W	C
56	n-Pentatriacontane	00630-07-9	standard	W	C
57	Naphthalene	00091-20-3	standard	W	C
58	Fluorene	00086-73-7	standard	W	C
59	Dibenzothiophene	00132-65-0	standard	W	C
60	Phenanthrene	00085-01-8	standard	W	C
61	Fluoranthene	00206-44-0	standard	W	C
62	Pyrene	00129-00-0	standard	W	C
63	Chrysene	00218-01-9	standard	W	C
64	Benzo(b)fluoranthene	00205-99-2	standard	W	C
65	Benzo(k)fluoranthene	00207-08-9	standard	W	C
66	Benzo(e)pyrene	00192-97-2	standard	W	C
67	Benzo(a)pyrene	00050-32-8	standard	W	C
68	Perylene	00198-55-0	standard	W	C
69	Indeno(1,2,3-cd)pyrene	00193-39-5	standard	W	C
70	Dibenzo(a,h)anthracene	00053-70-3	standard	W	C
71	Benzo(g,h,i)perylene	00191-24-2	standard	W	C

72	Pristane	01921-70-6	standard	W	C
73	Phytane	00638-36-8	standard	W	C
74	Anthracene	00120-12-7	standard	W	C
75	Benzo[b]naphtho[2,1[d]thiophene	239-35-0	standard	W	C
76	5b-Cholestane	481-20-9	standard	W	C
77	5a-Androstane	438-22-2	standard	W	C
78	Hopane	1176-44-9	standard	W	C
79	D22 n-Decane	16416-29-8	standard	W	C
80	D34 n-Hexadecane	15716-08-2	standard	W	C
81	D42 n-Eicosane	62369-67-9	standard	W	C
82	D62 n-Triacontane	93952-07-9	standard	W	C
83	D8-Naphthalene	1146-65-2	standard	W	C
84	D10-Anthracene	1719-06-8	standard	W	C
85	D12-Chrysene	1719-03-5	standard	W	C
86	D12-Perylene	1520-96-3	standard	W	C
87	D36-Heptadecane	39756-35-9	standard	W	C
88	D50-Tetracosane	16416-32-3	standard	W	C
89	D66-Dotriacontane	62369-68-0	standard	W	C
90	D10-1-methylnaphthalene	1517-22-2	standard	W	C
91	D10-Phenanthrene	1517-22-2	standard	W	C
92	D10-Pyrene	1718-52-1	standard	W	C
93	Ph buffers 4, 7, and 10	Varies	Calibration	S	C
94	Nitric Acid	7697-37-2	pH adjustment/ sand washing	Neutralize 6 < pH < 9	C
95	Methanol	67-56-1	fluorometry	W	C
96	Rhodamine B	81-88-9	fluorometry	W	C
97	Ethylene Glycol	107-21-1	fluorometry	W	C
98	Quinine Sulfate Dihydrate	6119-70-6	fluorometry	W	C
99	Sulfuric Acid	7664-93-9	Fluorometry, pH adjustment	Neutralize 6 < pH < 9	C
100	Dimethyldichlorosilane (5%) in Toluene		Silanizing glassware	W	C
101	Sodium Azide		Microbial Growth Inhibitor	W	C
102	Magnesium Sulfate		Media	S or T	C
103	Manganese Sulfate		Media	S or T	C
104	Boric Acid		Media	S or T	C
105	Zinc Sulfate		Media	S or T	C
106	Ammonium Molybdate		Media	S or T	C
107	Potassium Hydrogen Phosphate		Media	S or T	C
108	Potssium dihydrogen Phosphate		Media	S or T	C

109					
110					
111					
112					
113					
114					
115					
116					
117					
118					

Current Inventory of Crude Oils Line Item # 3 (May 2015)		
Anadarko	Endicott	Prudhoe Bay
ANS	Endicott (18% evaporated)	PXP 01
ANS 521	Esgravos	PXP 02
Arabian Light	FO2	Rock
BHP Billiton	Fuel 6	South Louisiana
Bonnie Light	Harmony	Sweet Synthetic
Bunker C	IFO 120	Terra Nova
Dilbit, Cold Lake	IFO 380	Venoco E-10
Dilbit, WCS	North Star	Venoco E-19
Doba	PER 038	
Elly	PER 040	

Current Inventory of Oil Spill Dispersants Line Items # 10-15 (May 2015)		
Accell Clean DWD	Finasol OSR52	Nokomis 3-F4
Biodispers	JD-2000	Saf-Ron Gold
Corexit 9500	NEOS AB3000	SX-100
Dispersit SPC1000	Nokomis 3-AA	ZI-400
FFT Solution		

Current Inventory of Oil Spill Surface Washing Agents Line Items # 4-9 (May 2015)		
ADP7	F500	Petroluxus
Aquaclean	Gold Crew SW	Petrotech 25
BG-Clean 401	Green Beast	Premier 99
Biosolve	Jep Marine Clean	Procleans PCR 107
CleanGreen Planet Wash	Marine Green Clean	Sandklene 950
Corexit 9580	Marine Green Clean Plus	SC-1000
Cytosol	Naturama G3 A-5	Simple Green
Dynamic Green	Nokomis 5W	Spillclean
Enviroclean	Nontox SWA	Superall #38
EPA Oil Field Solution™	Petro-Clean	

Biological Research

Does the project in any way involve manipulation of recombinant DNA?	No
If yes, are all proposed activities specifically exempted from the NIH Guidelines for Research Involving Recombinant DNA Molecules?	

Does the project in any way involve human subjects or biological materials obtained from human subjects?	No
If yes, is the project exempt from the Health and Human Services Policy for Protection of Human Subjects?	
Does the project involve animals requiring Institutional Animal Care & Use Committee (IACUC) approval? (includes vertebrate & invertebrates animals)	No

Biological Agents

(The Biosafety Level (BSL) and Animal Biosafety Level (ABSL) refer to specific combinations of work practices, safety equipment, and facility design elements utilized to minimize exposure of workers and the environment to infectious agents. Principal Investigators must perform an agent risk assessment to determine the BSL.)

Item #	Biological Agent (list all that apply)	BSL #	Source of Biological Agent	Vaccination Required?
1	Oil degrading bacteria isolated from environmental samples	1	Water or sediments	no

Waste Management

DCM, hexane, methanol, and crude oil wastes (dissolved in DCM) from analytical samples collected via separatory funnel, standards, and glassware rinsate should be disposed of through the SHEM hazardous wastes program due to solvent, oil and PAH contents. After washing gravel and sand with DCM, the DCM is drained into the waste container and the substrate is placed in the fume hood to allow the remaining DCM to evaporate off, before disposing of the cleaned substrate in the garbage.

Spent silanizing solution should be disposed throught the SHEM hazardous waste program.

Original chemical reagents will be disposed as indicated in the chemical use table.

Any remaining fresh or seawater will be disposed of down the sink drain because no known hazardous wastes are involved.

Aqueous waste remaining after removal of DCM using a separatory funnel may be sink disposed. Any remaining DCM is placed in a hazardous waste container before dumping remaining water to sink.

Acid solution from sand/gravel cleaning will be collected and neutralized using sodium hydroxide to a pH between 5 and 9 and then disposed of down the sink.

Will Hazardous Waste Be Generated?   yes   Will the Treatability Exemption be Utilized?   no

Sample Management

All samples will be labeled with sample descriptors including date, analyst, and constituents (solutes and solvents). They will be stored in the refrigerators in 701 or CTR710. They will be kept until data is approved and then disposed of using the Chemical Waste Program. Any enriched bacterial consortia will be frozen and kept in the -80 freezer in 701. They may be maintained indefinitely.

Hexane containing samples are flammable and should only be stored in refrigerators or freezers designed and labeled as approved for flammable material storage.

Spill Response

General spills are handled in accordance with the Chemical Hygiene Plan found at
http://intranet.epa.gov/nerlintr/shem/lab_safety/docs/ChemHygiene.pdf

Small spills shall be wiped up by project personnel wearing proper PPE and the absorbent material bagged, labeled as to its hazardous constituents, then submitted to the SHEM Waste Program for proper disposal. In the event of a large solvent spill, SHEM will be contacted via x7997 or by way of security per the Chemical Hygiene Plan.

The spill of any bacterial consortia that have been enriched from environmental samples will be doused with either a 10% chlorine solution or 70% ethanol solution, allowed to sit for ~ 10 minutes and then wiped up. The wipes used will be placed in a biohazard bag for autoclaving.

The chemical spill kit is located: 701, 703, 708 - on the left side of the lab near the door. 710 – May use a spill kit from the other laboratories

Authorized Personnel

Training and medical monitoring requirements will vary depending on the complexity and materials used in the process. Therefore, only personnel trained and monitored will be permitted to work under this plan. To be "authorized", employees must have completed the training and screenings selected below.

Mandatory for all researchers	
Initial Laboratory Safety	X
Current Chemical Hygiene Plan Laboratory Safety Refresher	X
Hazardous Waste Management (RCRA)	X
Project/Task Dependent	
Medical Surveillance	X
Respiratory Protection	
Biosafety / Blood borne Pathogens	
Initial Field Safety and/or 8 hour field safety refresher training in the fiscal year	
40 - hour HAZWOPER and/or 8 hour HAZWOPER refresher in the last 12 months	
Hearing Protection	
First Aid / CPR / AED	
DOT Hazardous Materials Awareness/Shipment	
Radiation Safety	
EPA Driver's Training	
EPA Boat Safety Training	
EPA Nanomaterials Health and Safety Awareness Training	
Other (specify) – Dichloromethane information (See below)	X

References:

General Activities
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Room / Area	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Preparation of artificial seawater and freshwaters	703	Little chemical hazard as it consists of salts. Irritants	Prepare chemical solutions in a CFH where possible	Lab coat, safety glasses with side shields, nitrile gloves, closed-toe shoes
Use of freezer	701	Thermal burns from the ultra low freezer	Use caution when handling items from the freezer	Thermal protective gloves Lab coat, safety glasses with side shields, nitrile gloves, closed-toe shoes
Use of autoclave	380	See chemical hygiene plan for Autoclave Hazard Analysis	See chemical hygiene plan for Autoclave Hazard Analysis	See chemical hygiene plan for Autoclave Hazard Analysis
Use of centrifuge		See chemical hygiene plan for Centrifuge Hazard Analysis	See chemical hygiene plan for Centrifuge Hazard Analysis	See chemical hygiene plan for Centrifuge Hazard Analysis
Preparation of dilute acid from concentrated acid for performing pH adjustments	703	Splash – chemical burns to exposed skin	Prepare solution in a chemical fume hood	Face shield – Lab coat, safety glasses with side shields, nitrile gloves, closed-toe shoes
Use of drying oven and muffle furnace	703	Burns	Caution with hot glassware. Let muffle furnace completely cool down before removing glassware.	Thermal protective gloves
CTR 710		Limited ventilation – build up of chemical vapors, inhalation of DCM and other toxic and carcinogenic chemical vapors	No open chemical container work should be performed in CTR 710. All containers should remain closed. Samples should be moved to a room with a CFH if necessary to open.	Lab coat, safety glasses with side shields, nitrile gloves, closed-toe shoes

Job Hazard Analysis
SOP 1 Glassware Washing

Glassware Washing			
* includes supplies, utensils and containers in contact with soil, extraction fluid, and/or leachate			
Sequence of Basic Job Steps	**Potential Hazards**	**Recommended Action or Procedure**	**PPE Required**
Rinse loose debris from the surface	- Cross contamination from glassware to personnel – potential exposure - Splash or spray from rinsing – potential exposure - Potential breakage of glassware from cracks or defects – cuts / lacerations / contamination	- Inspect glassware before cleaning for cracks or other damage – discard in broken glass container if damage is noticed or suspected - use low pressure water to avoid splash and/or aerosolization of the contaminants - if any glassware is broken during cleaning – only remote means should be used to pick up any broken glass	- minimum of safety glasses, laboratory coat, and gauntlet length nitrile gloves
Wash with brush, soap, and water. Triple rinse with water. Soak in soap bath.	- Cross contamination from glassware to personnel – potential exposure - Splash or spray from rinsing – potential exposure - Potential breakage of glassware from cracks or defects – cuts / lacerations / contamination	- Inspect glassware before cleaning for cracks or other damage – discard in broken glass container if damage is noticed or suspected - use low pressure water to avoid splash and/or aerosolization of the contaminants - if any glassware is broken during cleaning – only remote means should be used to pick up any broken glass	- minimum of safety glasses, laboratory coat, and gauntlet length nitrile gloves
Drying object using drying racks	- potential for dropping the glassware, tools, etc. – breakage, spillage, contact with other surfaces - slip / trip / fall hazards from water spillage or splashing from the rinsing process	- ensure that the drying racks are placed to reduce any ergonomic hazard from stretching, or repetitive motion - follow the established emergency procedures for injuries or spills including immediate notification of your supervisor or 911 for life threatening cases (also x7777, direct contact to security)	- minimum of safety glasses, laboratory coat, and gauntlet length nitrile gloves

SOP 2 -Preparation of a Surrogate Recovery Standard
Job Hazard Analysis, Controls, and PPE
SOP 3 - Preparation of Internal Standard Solution
Job Hazard Analysis, Controls, and PPE
SOP 4 - Preparation of Working Standards, Check Standards, and Oil Standards for GC/MS
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Weigh reagents Dissolve reagents / wash beakers using methylene chloride Transfer the solution	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	Prepare the reagents / standards in a chemical fume hood only. Handle reagents in the smallest quantities possible and do not cross contaminate. DCM – attempt to not 'pour' DCM as the ST is low and tends to spread. Use the sash on a CFH for splash protection where possible. Review OSHA Regulated Substance Awareness for DCM.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
Pipetting	see chemical hygiene plan for pipetting recommendations	See chemical hygiene plan for pipetting recommendations	Double nitrile gloves and / or silvershield gloves (where dexterity is not an issue). Lab coat, safety glasses with side shields, and closed-toe shoes.

SOP 5 - GC/MS Method for the Analysis of Crude Oil
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Compressed Gas Usage (Helium)	See Chemical Hygiene Plan – JHA for Compressed Gas Cylinders	See Chemical Hygiene Plan – JHA for Compressed Gas Cylinders	See Chemical Hygiene Plan – JHA for Compressed Gas Cylinders
Solvent / standard / stock preparation	See JHA for SOP 2, 3, and 4)	See JHA for SOP 2, 3, and 4)	See JHA for SOP 2, 3, and 4)
GC Operation	Compressed Gases GC venting of toxic analytes	Ensure GC exhaust is routed to laboratory ventilation.	Lab coat, safety glasses, protective gloves

SOPs
Analysis of Oil Concentration in DCM by UV/Vis Spectrophotometry and Spectrofluorometry
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Add DCM to crude oil Syringe use Extraction with DCM (shaking and venting) Dispense / transfer solutions	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	Prepare the reagents / standards in a chemical fume hood only. Handle reagents in the smallest quantities possible and do not cross contaminate. DCM – attempt to not 'pour' DCM as the ST is low and tends to spread. Use the sash on a CFH for splash protection where possible. Review OSHA Regulated Substance Awareness for DCM.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
Pipetting	See chemical hygiene plan for pipetting recommendations	See chemical hygiene plan for pipetting recommendations	Double nitrile gloves and / or silvershield gloves (where dexterity is not an issue). Lab coat, safety glasses with side shields, and closed-toe shoes.
Operation of Spectrophotometer and Fluorometer	UV light exposure	Ensure all equipment guards are present and operable.	Nitrile gloves Lab coat, safety glasses with side shields, and closed-toe shoes.

SOP
The Baffled Flask Test for Determining Effectiveness of Dispersants
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Add DCM to crude oil and seawater Syringe use Extraction with DCM (shaking and venting) Dispense / transfer solutions	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	Prepare the reagents / standards in a chemical fume hood only. Handle reagents in the smallest quantities possible and do not cross contaminate. DCM – attempt to not 'pour' DCM as the ST is low and tends to spread. Use the sash on a CFH for splash protection where possible. Review OSHA Regulated Substance Awareness for DCM.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
Pipetting	See chemical hygiene plan for pipetting recommendations	See chemical hygiene plan for pipetting recommendations	Double nitrile gloves and / or silvershield gloves (where dexterity is not an issue). Lab coat, safety glasses with side shields, and closed-toe shoes.
Extraction with DCM including shaking and venting	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for	Perform extraction in a chemical fume hood only. Handle reagents in the smallest quantities possible and do not cross contaminate. Use the sash on a CFH	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side

	illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	for splash protection where possible. This should **ONLY** be done in a CFH.	shields, and closed-toe shoes.
Operation of Spectrophotometer or Spectrofluorometer	UV light exposure	Ensure all equipment guards are present and operable.	Nitrile gloves Lab coat, safety glasses with side shields, and closed-toe shoes.
Use of the shaker	Spills, mechanical issues with equipment	Ensure all equipment guards are present and operable. Ensure a periodic inspection of equipment.	Nitrile gloves Lab coat, safety glasses with side shields, and closed-toe shoes.

SOP - Natural Substrate Protocol
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Acid wash of the substrate	burns from acid contact from spills, splashes from bath	Conduct in chemical fume hood	Double nitrile gloves - Wear normal length nitrile gloves inside of elbow length nitrile gloves; Wear a face shield / chemical splash goggles.
Addition of crude oil	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn) – see chemical hygiene plan for pipetting recommendations	Prepare the reagents / standards in a chemical fume hood only. Handle reagents in the smallest quantities possible and do not cross contaminate. Use the sash on a CFH for splash protection where possible. – see chemical hygiene plan for pipetting recommendations. Review OSHA Regulated Substance Awareness information below for DCM.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
Use of the shaker	skin chemical contact from splash or spill - eye chemical contact inhalation of chemicals contact injury with moving/rotating machinery	Work in a chemical fume hood when preparing reagents. Ensure all caps are tightly sealed. Ensure area is clear before starting shaker. Secure loose fitting clothing to prevent snagging by shaker.	Laboratory coat, and nitrile gloves; wear chemical splash goggles
DCM extraction	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	Perform extraction in a chemical fume hood only. Handle reagents in the smallest quantities possible and do not to not cross contaminate. Use the sash on a CFH for splash protection where possible. This should **ONLY** be done in a CFH.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
UV spectrophotometry	eye chemical contact inhalation of chemicals skin chemical contact from splash or spill	Work in a chemical fume hood when handling reagents with respiratory warnings. Handle quartz cuvet with secure grip to prevent dropping or breaking	wear a laboratory coat, and nitrile gloves; wear chemical splash goggles

Methylene Chloride / Dichloromethane

Per OSHA regulation 29 CFR 1910.1052, an employer shall provide information and training for each affected employee prior to or at the time of initial assignment to a job involving potential exposure to methylene chloride. Through the use of laboratory fume hoods and procedures outlined in the laboratory chemical hygiene plan and the project health and safety plan, exposure above the regulatory action level is not expected. A full copy of the regulation is available on the OSHA website at www.OSHA.gov or through the SHEM Office. Other information on the safe use of methylene chloride is also available from the SHEM office and OSHA website.

DICHLOROMETHANE	**ICSC: 0058**
Methylene chloride DCM CH_2Cl_2 Molecular mass: 84.9 ICSC # 0058	CAS # 75-09-2 RTECS # PA8050000 UN # 1593 EC # 602-004-00-3 Decemb er 04, 2000 Validated

TYPES OF HAZARD/ EXPOSURE	ACUTE HAZARDS/ SYMPTOMS	PREVENTION	FIRST AID/ FIRE FIGHTING
FIRE	Combustible under specific conditions. Gives off irritating or toxic fumes (or gases) in a fire.		In case of fire in the surroundings: use appropriate extinguishing media.
EXPLOSION	Risk of fire and explosion (see Chemical Dangers).	Prevent build-up of electrostatic charges (e.g., by grounding).	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE		PREVENT GENERATION OF MISTS! STRICT HYGIENE!	
●INHALATION	Dizziness. Drowsiness. Headache. Nausea. Weakness. Unconsciousness. Death.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Artificial respiration may be needed. Refer for medical attention.
●SKIN	Dry skin. Redness. Burning sensation.	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse and then wash skin with

			water and soap.
•EYES	Redness. Pain. Severe deep burns.	Safety goggles , face shield or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
•INGESTION	Abdominal pain. (Further see Inhalation).	Do not eat, drink, or smoke during work. Wash hands before eating.	Rinse mouth. Do NOT induce vomiting. Give plenty of water to drink. Rest.

SPILLAGE DISPOSAL	STORAGE	PACKAGING & LABELLING
Personal protection: filter respirator for organic gases and vapours. Do NOT let this chemical enter the environment. Ventilation. Collect leaking and spilled liquid in sealable containers as far as possible. Absorb remaining liquid in sand or inert absorbent and remove to safe place.	Separated from metals (see Chemical Dangers), food and feedstuffs . Cool. Ventilation along the floor.	Do not transport with food and feedstuffs. Xn symbol R: 40 S: (2-)23-24/25-36/37 UN Hazard Class: 6.1 UN Packing Group: III

| I M P O R T A | PHYSICAL STATE; APPEARANCE: COLOURLESS LIQUID , WITH CHARACTERISTIC ODOUR. PHYSICAL DANGERS: The vapour is heavier than air. As a result of flow, agitation, etc., electrostatic charges can be generated. CHEMICAL DANGERS: On contact with hot surfaces or flames this substance decomposes forming toxic and corrosive fumes. Reacts violently with metals such as aluminium powder and magnesium powder, strong bases and strong oxidants causing fire and explosion hazard. Attacks some forms of plastic rubber and coatings. | ROUTES OF EXPOSURE: The substance can be absorbed into the body by inhalation and by ingestion. INHALATION RISK: A harmful contamination of the air can be reached very quickly on evaporation of this substance at 20°C. EFFECTS OF SHORT-TERM EXPOSURE: The substance is irritating to the eyes , the skin and the respiratory tract . Exposure could cause lowering of consciousness. Exposure could cause the formation of methaemoglobin. EFFECTS OF LONG-TERM OR REPEATED |

N		EXPOSURE:
T	**OCCUPATIONAL EXPOSURE LIMITS:**	Repeated or prolonged contact with skin may cause
	TLV: 50 ppm as TWA; A3 (confirmed animal carcinogen	dermatitis. The substance may have effects on the central
	with unknown relevance to humans); BEI issued; (ACGIH	nervous system and liver . This substance is possibly
D	2004).	carcinogenic to humans.
	MAK:	
	Carcinogen category: 3A;	
A	(DFG 2004).	
	OSHA PEL: 1910.1052 TWA 25 ppm ST 125 ppm	
T	NIOSH REL: Ca See Appendix A	
	NIOSH IDLH: Ca 2300 ppm See: 75092	
A		

PHYSICAL PROPERTIES	Boiling point: 40°C Melting point: -95.1°C Relative density (water = 1): 1.3 Solubility in water, g/100 ml at 20°C: 1.3 Vapour pressure, kPa at 20°C: 47.4	Relative vapour density (air = 1): 2.9 Relative density of the vapour/air-mixture at 20°C (air = 1): 1.9 Auto-ignition temperature: 556°C Explosive limits, vol% in air: 12-25 Octanol/water partition coefficient as log Pow: 1.25
ENVIRONMENTAL DATA	This substance may be hazardous in the environment; special attention should be given to ground water contamination.	

NOTES

Addition of small amounts of a flammable substance or an increase in the oxygen content of the air strongly enhances combustibility. Depending on the degree of exposure, periodic medical examination is suggested. The odour warning when the exposure limit value is exceeded is insufficient. Do NOT use in the vicinity of a fire or a hot surface, or during welding. R30 is a trade name. Card has been partly updated in April 2005. See section Occupational Exposure Limits.

Transport Emergency Card: TEC (R)-61S1593

NFPA Code: H2; F1; R0;

ADDITIONAL INFORMATION

IMPORTANT LEGAL NOTICE:	Neither NIOSH, the CEC or the IPCS nor any person acting on behalf of NIOSH, the CEC or the IPCS is responsible for the use which might be made of this information. This card contains the collective views of the IPCS Peer Review Committee and may not reflect in all cases all the detailed requirements included in national legislation on the subject. The user should verify compliance of the cards with the relevant legislation in the country of use. The only modifications made to produce the U.S. version is inclusion of the OSHA PELs, NIOSH RELs and NIOSH IDLH values.

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Peter EGAN
Sent: Mon 4/18/2016 2:48:02 PM
Subject: Out of Office: purchase of Finasol OSR52

Hi

I am sorry but I am now out of the office until Monday 11th April. I will have (intermittent) access to Email over this period.

If you need to speak to someone during my absence, Darvin Dwyer (darvin.dwyer@total.com) can be contacted on 713 969 4610.

Best regards,

Peter Egan

Cell: +1 713 297 1996

To: Gilliland, Alice[Gilliland.Alice@epa.gov]; McClellan, Kim[Mcclellan.Kim@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Schubauer-Berigan, Joseph
Sent: Tue 9/15/2015 9:19:22 PM
Subject: RE: IMPORTANT - NEW STICS Entries

Yes, I will clear them at the branch level.

Joseph P. Schubauer-Berigan, Ph.D.
Chief, Environmental Stressors Management Branch
USEPA, Office of Research and Development
National Risk Management Research Laboratory
26 W. Martin Luther King Drive
Cincinnati, OH 45268
schubauer-berigan.joseph@epa.gov
Voice 513-569-7734
FAX 513-569-7620

From: Gilliland, Alice
Sent: Tuesday, September 15, 2015 4:59 PM
To: McClellan, Kim; Schubauer-Berigan, Joseph
Cc: Conmy, Robyn
Subject: RE: IMPORTANT - NEW STICS Entries

Bryan is listed as the author, but I assume these are Robyn's?

Yes, I can review them later this week.

From: McClellan, Kim
Sent: Tuesday, September 15, 2015 4:57 PM
To: Schubauer-Berigan, Joseph; Gilliland, Alice
Cc: Conmy, Robyn
Subject: IMPORTANT - NEW STICS Entries

Hi Joe and Alice,

TIM ApprovalDyson	Brian	Devi Sundaravadivelu	ORD-013921	Evaluation of Sorbent and Solidifier Properties and their Impact on Oil Removal Efficiency	Abstract	9/11/2015 4:43 PM
TIM ApprovalDyson	Brian	Mobing Zhuang	ORD-013917	Biodegradability of Dispersed Heavy Fuel Oil at 5 and 25 C	Abstract	9/11/2015 4:28 PM
TIM ApprovalDyson	Brian	Yu Zhang	ORD-013915	Biodegradation of Finasol OSR 52 and Dispersed Alaska North Slope Crude Oil at 5 C and 25 C	Abstract	9/11/2015 3:34 PM
TIM ApprovalDyson	Brian	Ruta Deshpande	ORD-013912	Biodegradability Of Diluted Bitumen Oil By Kalamazoo River Cultures In Freshwater	Abstract	9/11/2015 2:57 PM

The abstracts are due to the GoMRI Gulf Oil Spill and Ecosystem Science Conference on Thursday. Can these abstracts be reviewed and approved, so that they can be submitted on Thursday. I will be sending the abstracts, on Wednesday (9/16/2015), after Scott Jacobs completes the Internal Technical Reviews on each abstract.

Thanks,

Kim

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: King, Thomas L[Tom.King@dfo-mpo.gc.ca]
From: Robinson, Brian
Sent: Wed 7/8/2015 12:17:53 PM
Subject: RE: Quick update

Using a DOR 1:20 sounds good. I'd suggest we use 1:100 and 1:200 and then that will allow us to do a direct comparison to the ANS and IFO-120 treatments, and that gives us a total of 12 runs. We won't be starting these until July 20th, so there is some time if we want to change our minds.

Brian

From: Conmy, Robyn [mailto:Conmy.Robyn@epa.gov]
Sent: July-07-15 3:01 PM
To: Robinson, Brian
Subject: RE: Quick update

Hi Brian,

So glad to hear that all is going smoothly in this final push. Drinks are on me on the next visit!

As for the SLC experiments, I don't think there will be that much difference between 1:20 and 1:25. But I think we should opt for 1:20 since that is what the other BSEE experiments were and what the targets DOR was for the DWH spill. If you or Tom think different, I am open to changing this though. For the SLC experiment treatments, let me think through this today and I will let you know tomorrow. Again, open to any suggestions.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

```
Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)
```

conmy.robyn@epa.gov

From: Robinson, Brian [mailto:Brian.Robinson@dfo-mpo.gc.ca]
Sent: Tuesday, July 07, 2015 1:46 PM
To: Conmy, Robyn
Cc: King, Thomas L
Subject: Quick update

Hi Robyn,

I hope you and your family enjoyed the 4th of July weekend! Hopefully it wasn't too hot.

I just wanted to send you a quick update to let you know where we stand with the various aspects of the project.

1) The condensate experiments (7) are completed, and the analysis of chemistry samples should be completed in the next 1-2 weeks.

2) Michel and his two grad students were here for a week and they completed all of their measurements necessary for the Jet modelling.

3)   I have received the three prototype fluorometers from Wetlabs and am working with Satlantic to get them setup in our tank (power supplies, data acquisition etc). They should be ready to go by early next week.

4)   We are starting the Finasol experiments next week. There are 9 runs in total and we should be able to complete them by July 17th.

That leaves us with the MC252 experiments. I was wondering what DOR you would like to test? In the ES&T paper, we used a DOR of 1:25, but for the BSEE project we have been using 1:20, 1:100 and 1:200. And did you want to use Corexit and/or Finasol? I can commit to about 12 experiments, so I'll let you choose what treatments you would like us to test.

Also, I believe Claire has the Horiba pretty much ready to go. We have a number of frozen samples in our freezer from last years experiments. Would you like me ask Claire to run EEMs on those samples?

Thanks,

Brian

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: King, Thomas L[Tom.King@dfo-mpo.gc.ca]
From: Robinson, Brian
Sent: Tue 7/7/2015 5:46:19 PM
Subject: Quick update

Hi Robyn,

I hope you and your family enjoyed the 4th of July weekend! Hopefully it wasn't too hot.

I just wanted to send you a quick update to let you know where we stand with the various aspects of the project.

1)   The condensate experiments (7) are completed, and the analysis of chemistry samples should be completed in the next 1-2 weeks.

2)   Michel and his two grad students were here for a week and they completed all of their measurements necessary for the Jet modelling.

3)   I have received the three prototype fluorometers from Wetlabs and am working with Satlantic to get them setup in our tank (power supplies, data acquisition etc). They should be ready to go by early next week.

4)   We are starting the Finasol experiments next week. There are 9 runs in total and we should be able to complete them by July 17th.

That leaves us with the MC252 experiments. I was wondering what DOR you would like to test? In the ES&T paper, we used a DOR of 1:25, but for the BSEE project we have been using 1:20, 1:100 and 1:200. And did you want to use Corexit and/or Finasol? I can commit to about 12 experiments, so I'll let you choose what treatments you would like us to test.

Also, I believe Claire has the Horiba pretty much ready to go. We have a number of frozen samples in our freezer from last years experiments. Would you like me ask Claire to run EEMs on those samples?

Thanks,

Brian

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Bryan, Elisha[Bryan.Elisha@epa.gov]
From: Holder, Edith
Sent: Fri 4/17/2015 2:44:24 PM
Subject: RE: Accell Clean DWD

We have ~2 mLs, which at 4 ul a test would be quite a few tests.

You must be working at home today as it was dark when I walked to your office to actually do 'show and tell.'

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Conmy, Robyn
Sent: Friday, April 17, 2015 9:45 AM
To: Holder, Edith
Subject: RE: Accell Clean DWD

Odd that they don't have any in stock. We currently don't have any in the lab correct?

We have 3 birthday parties, soccer, and piano this weekend. Sigh. Weekends are no longer restful....

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Holder, Edith
Sent: Friday, April 17, 2015 9:41 AM
To: Conmy, Robyn
Cc: Bryan, Elisha
Subject: FW: Accell Clean DWD

Do we want this if it is not part of a production lot?

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Bryan, Elisha
Sent: Friday, April 17, 2015 8:23 AM
To: Holder, Edith
Subject: Re: Accell Clean DWD

Hi Edie,

The ZI-400 company contacted me. They were wondering on when you need it by because they will have to make that small of a quantity up in the lab.

Any plans for this weekend? It looks like the weather is going to be really nice. We might go to Earth Day at Sawyer Point.

Thanks,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: Holder, Edith
Sent: Thursday, April 16, 2015 4:34 PM
To: Bryan, Elisha
Subject: RE: Accell Clean DWD

Thank you for following up on this.

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Bryan, Elisha
Sent: Thursday, April 16, 2015 3:50 PM
To: Holder, Edith
Subject: Re: Accell Clean DWD

Hi Edie,

No I have not heard from the manufacturers. I did try different email addresses for both of those companies last Friday. Maybe if I do not here from them by tomorrow I will give them a call. I just prefer email since it is a lot easier to track.

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: Holder, Edith
Sent: Thursday, April 16, 2015 2:53 PM
To: Bryan, Elisha; Conmy, Robyn
Subject: Accell Clean DWD

Greetings,

The above dispersant was received today.

Elisha, Robyn is hoping that we will be able to obtain Saf-Ron Gold and ZI-400. Have you heard anything from their manufacturers?

Thanks,

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Mike Fulton - NOAA Federal
Sent: Mon 7/6/2015 6:38:21 PM
Subject: Re: following up

Thanks Robyn. How about tomorrow at 11:30?
Mike

On Mon, Jul 6, 2015 at 1:29 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hi Mike,

I am in this week but out next week. I have time on Tuesday between 11-2 ET and
Wednesday anytime in the morning.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Monday, July 06, 2015 1:24 PM

To: Conmy, Robyn
Subject: Re: following up

Hi Robyn,

I hope you're well and had a great holiday. Would you have time for a chat about shoreline cleaners sometime in the next several days? Thanks.

Mike

On Mon, Feb 9, 2015 at 2:48 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

OK. If you are running behind, then we can try for Wednesday...

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Monday, February 09, 2015 2:28 PM

To: Conmy, Robyn
Subject: Re: following up

Thanks Robyn. I have another meeting in the morning, but I'll try to call at 10:30.

Mike

On Mon, Feb 9, 2015 at 2:24 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hi Mike,

I am available tomorrow morning between 9:30 -11 am ET.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Monday, February 09, 2015 10:15 AM
To: Conmy, Robyn
Subject: Re: following up

Hi Robyn,

I hope you're well. Would you have time for a quick call sometime this week? I've got a couple of dispersant (finasol, corexit) questions.

Mike

On Tue, Sep 23, 2014 at 11:18 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

> Thanks Robyn. I think we are about to receive the oil we requested from BP. Fingers crossed.
>
> Mike

On Fri, Sep 19, 2014 at 10:13 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

> Hi Mike,
>
>
> I heard from EPA OEM that the oil purchase is approved but that it hasn't been ordered. That is the only information I have received. I did speak with Debbie Payton on Wednesday and she mentioned that her office has gotten some oil that may be available to you. I hope that is the case. There is some irony that we are all trying to conduct oil research that is critical for regulation, yet cannot access the oil. Sigh.
>
>
>
> Cheers,
>
> Robyn
>
>
> <>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>
>
> Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--
Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief
Center for Coastal Environmental Health and
Biomolecular Research (CCEHBR)
USDOC/NOAA/NOS/NCCOS
219 Fort Johnson Road
Charleston, SC 29412-9110
voice: (843) 762-8576 fax: (843) 762-8700
e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

To: Mandsager, Kathy[kathy.mandsager@unh.edu]
From: Mandsager, Kathy
Sent: Thur 3/10/2016 6:38:20 PM
Subject: FW: State-of-Science for Dispersants Use in Arctic Water: Degradation & Fate Group
2016.02.25_Degradation and Fate with appendices for panel final review.docx

Reminder…. Due on Monday.

From: Mandsager, Kathy
Sent: Thursday, February 25, 2016 5:50 PM
Subject: State-of-Science for Dispersants Use in Arctic Water: Degradation & Fate Group

Dear Panel:

We would very much appreciate your review of this final version of the *Degradation and Fate* document. This document incorporates the edits and suggestions made via email and final discussion.

If you could reply by email with your approval of this document by **Monday, March 17** (2 weeks for this review) that would be greatly appreciated. I will need each of you that participated in this discussion to reply in the affirmative that you approve this document.

Please also confirm that your name and affiliation are listed correctly at the end of this document.

You deserve kudos for this great accomplishment! Thank you very much!

Kathy Mandsager

Program Coordinator

Coastal Response Research Center

Center for Spills and Environmental Hazards

234 Gregg Hall, Colovos Rd

University of New Hampshire

Durham, NH 03824

603.862.1545

To: Bryan, Elisha[Bryan.Elisha@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Holder, Edith
Sent: Mon 3/2/2015 7:41:51 PM
Subject: RE: List on shared drive

Elisha,

We received a liter of Finasol OSR 52 within the last year, so we probably don't need that one.

We have close to a L of Dispersit SPC 1000, but it is approaching 10 years old. We have Corexit 9500 from 2010 (approx. 50 mL). There is approx. 20 mL of old JD2000. Then there are small amounts (<2 mL) of Sea Brat, ZI400, Nokomis 3F4, and Saf-ron Gold.

I would say contact everyone except the manufacturers of Finasol, but Robyn can weigh in with her opinion. Robyn should have the opportunity to edit the product request email prior to sending.

Linda Whiteley (MARINE D-BLUE CLEAN™) called me a couple of weeks ago asking about our SWA results. After telling her that we had no results ready for release, I told her that we would be doing more dispersant testing and that I would like to include her product in our testing. So perhaps the note to her could mention that.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

Hi Edie,

I made the list and put it on the shared drive:

L:\Public\NRMRL-PUB\Holder\OilSpill

6 of the 19 listed are companies that we have previously tried to contact about SWA and either wanted us to sign an agreement or never responded. Another one has not gotten updated contact information and the company is in Japan. I highlighted these, maybe we already have them in the lab. Most of these do not seem to have a shelf life, do we still want to get new stuff if we already have it?

I can work on the email draft next week.

Have a nice weekend!

Elisha

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Bryan, Elisha[Bryan.Elisha@epa.gov]
From: Holder, Edith
Sent: Fri 4/17/2015 1:40:35 PM
Subject: FW: Accell Clean DWD

Do we want this if it is not part of a production lot?

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Bryan, Elisha
Sent: Friday, April 17, 2015 8:23 AM
To: Holder, Edith
Subject: Re: Accell Clean DWD

Hi Edie,

The ZI-400 company contacted me. They were wondering on when you need it by because they will have to make that small of a quantity up in the lab.

Any plans for this weekend? It looks like the weather is going to be really nice. We might go to Earth Day at Sawyer Point.

Thanks,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: Holder, Edith
Sent: Thursday, April 16, 2015 4:34 PM
To: Bryan, Elisha
Subject: RE: Accell Clean DWD

Thank you for following up on this.

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Bryan, Elisha
Sent: Thursday, April 16, 2015 3:50 PM
To: Holder, Edith
Subject: Re: Accell Clean DWD

Hi Edie,

No I have not heard from the manufacturers. I did try different email addresses for both of those companies last Friday. Maybe if I do not here from them by tomorrow I will give them a call. I just prefer email since it is a lot easier to track.

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: Holder, Edith
Sent: Thursday, April 16, 2015 2:53 PM
To: Bryan, Elisha; Conmy, Robyn
Subject: Accell Clean DWD

Greetings,

The above dispersant was received today.

Elisha, Robyn is hoping that we will be able to obtain Saf-Ron Gold and ZI-400. Have you heard anything from their manufacturers?

Thanks,

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Mike Fulton - NOAA Federal
Sent: Mon 7/6/2015 5:24:04 PM
Subject: Re: following up

Hi Robyn,

I hope you're well and had a great holiday. Would you have time for a chat about shoreline cleaners sometime in the next several days? Thanks.

Mike

On Mon, Feb 9, 2015 at 2:48 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

OK. If you are running behind, then we can try for Wednesday...

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Monday, February 09, 2015 2:28 PM

To: Conmy, Robyn
Subject: Re: following up

Thanks Robyn. I have another meeting in the morning, but I'll try to call at 10:30.

Mike

On Mon, Feb 9, 2015 at 2:24 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hi Mike,

I am available tomorrow morning between 9:30 -11 am ET.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Monday, February 09, 2015 10:15 AM
To: Conmy, Robyn
Subject: Re: following up

Hi Robyn,

I hope you're well. Would you have time for a quick call sometime this week? I've got
a couple of dispersant (finasol, corexit) questions.

Mike

On Tue, Sep 23, 2014 at 11:18 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

> Thanks Robyn. I think we are about to receive the oil we requested from BP.
> Fingers crossed.
>
> Mike
>
>
> On Fri, Sep 19, 2014 at 10:13 AM, Conmy, Robyn <Conmy.Robyn@epa.gov>
> wrote:
>
>> Hi Mike,
>>
>>
>> I heard from EPA OEM that the oil purchase is approved but that it hasn't
>> been ordered. That is the only information I have received. I did speak with
>> Debbie Payton on Wednesday and she mentioned that her office has gotten
>> some oil that may be available to you. I hope that is the case. There is some
>> irony that we are all trying to conduct oil research that is critical for
>> regulation, yet cannot access the oil. Sigh.
>>
>>
>>
>> Cheers,
>>
>> Robyn
>>
>>
>> <>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>
>>
>> Robyn N. Conmy, Ph.D.
>>
>> Research Ecologist
>>
>> USEPA/NRMRL/LRPCD
>>
>> 26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--
Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief
Center for Coastal Environmental Health and
Biomolecular Research (CCEHBR)
USDOC/NOAA/NOS/NCCOS
219 Fort Johnson Road
Charleston, SC 29412-9110
voice: (843) 762-8576 fax: (843) 762-8700
e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

To: Bryan, Elisha[Bryan.Elisha@epa.gov]; Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Holder, Edith
Sent: Thur 4/16/2015 6:53:51 PM
Subject: Accell Clean DWD

Greetings,

The above dispersant was received today.

Elisha, Robyn is hoping that we will be able to obtain Saf-Ron Gold and ZI-400. Have you heard anything from their manufacturers?

Thanks,

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Mike Fulton - NOAA Federal
Sent: Mon 2/9/2015 7:27:53 PM
Subject: Re: following up

Thanks Robyn. I have another meeting in the morning, but I'll try to call at 10:30.
Mike

On Mon, Feb 9, 2015 at 2:24 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hi Mike,

I am available tomorrow morning between 9:30 -11 am ET.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Monday, February 09, 2015 10:15 AM
To: Conmy, Robyn
Subject: Re: following up

Hi Robyn,

I hope you're well. Would you have time for a quick call sometime this week? I've got a couple of dispersant (finasol, corexit) questions.

Mike

On Tue, Sep 23, 2014 at 11:18 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

> Thanks Robyn. I think we are about to receive the oil we requested from BP. Fingers crossed.
>
> Mike
>
>
> On Fri, Sep 19, 2014 at 10:13 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:
>
>> Hi Mike,
>>
>>
>> I heard from EPA OEM that the oil purchase is approved but that it hasn't been ordered. That is the only information I have received. I did speak with Debbie Payton on Wednesday and she mentioned that her office has gotten some oil that may be available to you. I hope that is the case. There is some irony that we are all trying to conduct oil research that is critical for regulation, yet cannot access the oil. Sigh.
>>
>>
>> Cheers,
>>
>> Robyn
>>
>>
>> <>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>
>>
>> Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

Biomolecular Research (CCEHBR)

USDOC/NOAA/NOS/NCCOS

219 Fort Johnson Road

Charleston, SC 29412-9110

voice: (843) 762-8576 fax: (843) 762-8700

e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--
Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief
Center for Coastal Environmental Health and
Biomolecular Research (CCEHBR)
USDOC/NOAA/NOS/NCCOS
219 Fort Johnson Road
Charleston, SC 29412-9110
voice: (843) 762-8576 fax: (843) 762-8700
e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

Prediction of Droplet Size Distribution from Subsurface Oil Releases with and without Chemical Dispersants

Report Prepared for

Centre for Offshore Oil, Gas and Energy Research
Fisheries and Oceans Canada
Bedford Institute of Oceanography
Dartmouth, NS, Canada

Fisheries and Oceans   Pêches et Océans
Canada   Canada

By

Haibo Niu and Linlu Weng

Water Studies Laboratory
Department of Engineering
Dalhousie University (Truro Campus)
Truro, NS, Canada

DALHOUSIE
UNIVERSITY

September 5, 2015

Executive Summary

Oil and gas exploration and recovery activities increased in deeper water in last decades. During these exploration and recovery activities, subsurface oil blowout or leakage may occur. Even though it does not occur commonly as surface oil spill caused by transportation, the potential risk of subsurface oil spill is still highly concerned by scientists and public. However, it is more complex to understand the fate of spilled oil from deep depth of water compare to surface or shallow subsurface oil spill, leading to more challenge to the simulation of oil transport and fate and eventually to the response to the response. During modelling of oil spill from deepwater, prediction of the size distributions of oil droplets formed in subsea oil blowouts is very important because of their direct influence on the fate and transport of oil in the marine environment. However, both our knowledge on the droplet size distributions and our capability to predict the distributions are still limited. One of the most recent and promising approaches for the distributions of droplet size is the Modified Weber Number approach developed by SINTEF. Such a method is based on experimental results with a certain type of oil. However, this approach has only been validated by light crude oil (Oseberg Blend crude oil). To validate this approach over a range of oil types, a series of experimental studies was conducted with a subsurface release of Intermediate Fuel Oil 120 (IFO-120) and Alaskan North Slope (ANS) crude oil in a horizontal flow tank located in the Bedford Institute of Oceanography, Canada.

Based on the droplet size obtain from the experiment, corresponding median droplet diameters (d_{50}) and the relative droplet size (d_{50}/D) were calculated. Accordingly, the relations between d_{50}/D and modified Weber number, Reynolds number, and oil concentration were quantified. With regression, the empirical coefficients for the prediction of droplets size distribution based on the modified Weber number were determined for a certain type of oil (e.g., IFO-120 and ANS). The results indicated that the chemical dispersant plays an importance role in reduce the droplet size of ANS no matter in spring or summer conditions. The effectiveness of dispersant in reducing droplet size is higher on ANS than which on IFO-120. There may be thresholds for the dose of chemical dispersant to some oils (e.g., IFO-120) but will need further experiments to analyze. There may also be over dose of dispersant to some oils (e.g., ANS) when the DOR is high, eventually affecting the droplet size distribution. Future experiment will also need for this particular issue. Furthermore, the data analysis has also indicated that the distributions of the data with $d/d_{50} <= 1$ and $d/d_{50} > 1$ are significantly varied. Therefore, a two-step Rosin-Rammler approach was introduced to more accurately predict the droplet size distribution. The regression coefficients for the two-step Rosin-Rammler are higher than which for the original single one in most of the case, indicating the advantage of the proposed two-step Rosin-Rammler approach.

It should also be noted that the measured IFT for the IFO-120 and ANS with different DORs appeared significant difference compared with the ones measured from SINTEF for the modified Weber number approach. This may due to the characteristics of different oil. Further experiments will be needed to address this issue.

i

Table of Contents

Table of Tables

Table of Figures

1 Introduction

The increased in offshore oil and gas exploration in deep waters increases the risk of deepwater oil spills. One recent example is the Deepwater Horizon (DWH) incident in the Gulf of Mexico. Oil released from subsurface blowouts breaks up into droplets and the sizes of these droplets have strong impacts on the subsequent fate of oil in the marine environment (Chen and Yapa, 2007; Bradvik et al., 2013; Johansen et al., 2013). With a density smaller than that of the ambient seawater, larger oil droplets will rise to the sea surface more rapidly than smaller droplets and will reach surface closer to the spill location than the smaller droplets. Better knowledge on droplet size distributions resulting from subsurface oil releases will help us predict whether the oil will surface and if so, when and where and what the oil slick thickness be (Chen and Yapa, 2003).

Currently, both our knowledge on the droplet size distributions and our capability to predict the distributions are limited. Before the DWH incident, only very few experimental work have been conducted to measure droplet size distribution from subsurface releases and only few studied the effects of chemical dispersant on droplet sizes. Topham (1975) was probably the earliest work studying droplets from subsurface releases and he has reported droplet size ranging from 0.5 mm (detection limit) to 3 mm for Norman Wells crude and a peak diameter of 15 µm for Swan Hills crude. The field experimental data from the Canadian Arctic gathered by Dome Petroleum gave a range from 50 µm to 2.1 mm (Buist et al., 1981). Masutani and Adams (2001) conducted jet experiments on an oil-water system using four types of crude oil and studied the different modes of jet breakup. Johansen et al. (2003) was the only full-scale deep water experiment, they observed that droplet sizes resulting from the release of diesel at 844 m depth were from 1 to 10 mm.

While DWH is the first oil spill occurring at significant depth (~1500m), it is also the first time where chemical dispersants were directly injected into the subsurface oil release to enhance the dispersion of oil over a large water column (Louis et al., 2011). A total of 18,379 barrels of dispersant were used at the DWH incident (The Federal Interagency Solutions Group, 2010). When a chemical dispersant is added at the depth of the wellhead, the surfactant is expected to break the oil into small droplets. The only available data on the effects of dispersant on droplet sizes is Brandvik et al. (2013). Brandvik et al (2013) have studied the effects of dispersant by using seven different dispersant-oil-ratios (DORs) and the peak droplet sizes were found strongly affected by DORs.

Very few publications are available on predicting the droplet sizes. Chen and Yapa (2007) developed a method based on the maximum entropy formalism using the "deepspill" experimental data. Currently, this method is mainly applied to subsurface releases without chemical dispersant. However, the feasibility of this method is yet to be validated in the case of subsurface release with chemical dispersant. More recently, Johansen et al. (2013) have incorporated new experimental data for the subsurface release cases with chemical dispersant application developed a modified Weber number approach to predict the droplet sizes. Zhao et al. (2014) used the same data set with a droplet breakup rate approach. However, all of these available approaches were based on one single set of experimental data on subsurface oil-dispersant interaction (Brandvik et al., 2013) by using one type of oil (Oseberg Blend). There is an urgent need to validate these models with extensive experimental data on more oil types.

Furthermore, although it appears likely that subsurface *in-situ* use of chemical dispersants may be very effective for countering deepwater oil spills, many uncertainties still exist. For example, assumptions of the optimum DOR are based on empirical data mostly obtained from bench-scale experimental protocols that have been designed for testing at standard temperatures and pressures (STP), whereas conditions at a wellhead on the ocean floor or anywhere along a riser beneath the ocean surface could be significantly different. Dispersant effectiveness as a function of dispersant type, oil type, and DOR must be better understood for application in deepwater environments. Furthermore, the interaction of dispersant and crude oil at depth under different turbulence regimes may also have significant implication in optimizing operational performance of subsurface dispersant injection. Improved understanding of these issues should provide better support in decision-making for subsurface dispersant application.

To fill the existing knowledge gaps, extensive experimental studies have been conducted in a flow-through wave tank located at the Bedford Institute of Oceanography (BIO) with an underwater high flow rate oil release system. Accordingly, the objective of this project is to: 1) analyze these newly gained experimental data from BIO; 2) develop a method that can effectively predict the droplet size distributions of oil released from subsurface, with and without application of chemical dispersant; and 3) incorporate the newly developed method with an oil spill model to study its effects on fate and transport of oil from subsurface releases.

2 Methodology

2.1 Maximum Entropy Formalism (MEF) Approach

Probability density function (PDF) such as Rosin-Rammler or Nukiyama-Tanasawa distribution, are established correlations for the droplet size distribution. However, more theoretical foundations were needed for these correlation. Maximum entropy formalism (MEF) approach was used by Chen and Yapa (2007) to develop model for estimating oil droplet size distribution.

To estimate a droplet spectrum, the probability density function (PDF) needs to be connected to a characteristic size (e.g. δ_{max}, δ_{30}, or δ_{32}) (Chen and Yapa, 2007). δ_{max} is the maximum droplet size, δ_{30} is the mass mean volume equivalent diameter, and δ_{32} is the Sauter mean (volume surface) diameter. δ_{max} is determined by diameter of the nozzle D and the Weber number (We) as follows:

$$\delta_{\max} = kDWe^{-3/5}$$

(1)

By knowing δ_{max}, δ_{30} and δ_{32} can be estimated as follows:

$$\delta_{30} = \left(\int_0^{\delta_{\max}} f \cdot \delta^3 d\delta \right)^{1/3}$$

(2)

$$\delta_{32} = \left(\int_0^{\delta_{\max}} f \cdot \delta^2 d\delta \right)^{-1} \delta_{30}^3$$

(3)

where f is PDF defined as:

$$f = 3\delta_1^2 \exp\left[-\lambda_0 - \lambda_1\delta_1 3 - \lambda_2\delta_1^3 u_1 - \lambda_3(\delta_1^3 u_1^2 + \delta_1^2 B) \right]$$

(4)

ii

Where δ_I is nondiamensional droplet diameter. u_I is nondimensional droplet velocity. After solving the Lagrangian multiplier λ_i (λ_0, λ_1, λ_2, λ_3), which are evaluated by several nonlinear constraint equations, mentioned in the Chen and Yapa (2007) the droplet size number based

$$f_N = \frac{dN}{d(\delta/\delta_{30})} = A\exp\left[-\frac{\delta_{30}}{\delta} - B\left(\frac{\delta}{\delta_{30}}\right)^C\right]$$

distribution can be obtained in Equation (5 (Chen and Yapa, 2007). It indicates that the droplet distributions are controlled by two tuning coefficients B and C:

$$f_N = \frac{dN}{d(\delta/\delta_{30})} = A\exp\left[-\frac{\delta_{30}}{\delta} - B\left(\frac{\delta}{\delta_{30}}\right)^C\right]$$

(5)

Where f_N is a number based probability density function, N is the droplet number, δ_{30} is the volume mean diameter, A is a term that accounts for normalization conditions. Their result seems to be less biased. Due to the limited data, the effects of oil properties were neglected. The applicability of the formulation for chemically dispersed oil will be tested in future study.

2.2 Droplet Breakup Approach

Maximum Entropy Formalism (MEF) Approach was widely used in flow atomization and spray; there is less of consideration of oil property. Zhao et al. (2014) has developed a VDROP-J model which considers the effects of both oil viscosity and oil-water interfacial tension (ITF). In a liquid-liquid dispersion system, a population balance equation is proposed as follows:

$$\frac{\partial n(d_i,t)}{\partial t} = \underbrace{\sum_{j=i+1}^{n} \beta(d_i,d_j)g(d_j)n(d_j,t)}_{\text{droplet breakup}}$$

$$+ \underbrace{\sum_{j=1}^{n}\sum_{k=1}^{n}\Gamma(d_j,d_k)n(d_j,t)n(d_k,t) - n(d_i,t)\sum_{j=i+1}^{n}\Gamma(d_i,d_j)n(d_j,t)}_{\text{droplet coalescene}}$$

(6)

Where n is number concentration of droplets of diameter d_i at a given time t. The term $\beta(d_i, d_j)$ is the breakage probability density function (dimensionless)for the creation of droplet of diameter d_i due to breakage of droplets of (a larger) diameter d_j, and $g(d_j)$ is the breakage frequency of droplets of diameter d_j. The first term represents the birth of droplets d_i resulting from the breakup of droplets d_j, while the second term represents the death of droplets d_i due to breakup into smaller droplets. For droplets coalescence, the term $\Gamma(d_k, d_j)$ is the coalescence rate (m³/s). The first term of droplet coalescence represents the birth of droplets d_i as a results of coalescence events occurring between droplets d_k and d_j to form drops with the size of d_i, while the second term represents deaths of droplets d_i due to the coalescence of drops d_i with all other drops (including drops of size d_i themselves) to form larger drops.
The breakage rate $g(d_i)$ is given by:

iii

$$g(d_i) = K_b \int_{n_e} S_{ed}(u_e^2 + u_d^2)^{1/2} BE \cdot dn_e \tag{7}$$

where S_{ed} represents the collisional cross section of eddy and droplet (m^2), u_e is the turbulent velocity of an eddy (m/s), u_d is droplet velocity (m/s), n_e is number concentration of eddies (number of eddies/m^3), BE is the breakup efficiency which is related with the IFT, dn_e is the number of eddies of size between μ_e and μ_d are the velocities of eddies and droplet and K_b is a system-dependent parameter for droplet breakup, and would need to be obtained by calibration to experimental data. Based on experimental data, the K_b was found can be approximated by (Zhao et al., 2014):

$$K_b = 3.57(\rho U^2 D)^{-0.63} \tag{8}$$

where ρ is density (kg/m^3), U is velocity (m/s), and D is droplet diameter (m) In Figure 1, an example is given for the comparison of VDROP-J with the experimental data (Brandvik et al., 2013). For a given release condition (e.g., same oil type, discharge nozzle size, and exit velocity), same K_b (0.11 in this case) will be obtained. Therefore, Equation 8 does not consider the effects of chemical dispersant on droplet sizes or shape of the curves. To fit the droplet size distributions with model, other parameters such as ITF or known dispersion efficiency must be used to adjust the shape of the curve. Both Zhao et al. (2014) and Johansen et al. (2013) indicated IFTs (15.5, 0.05 and 0.09) from three experiments based on DOR of 0, 1:50, and 1:25, respectively. The measured IFT (0.09) for DOR=1:25 is actually higher than the IFT (0.05) for DOR=1:50.This is against to the IFT fitting produced by Zhao et al. (2014) which indicated that the higher IFT would lead to a closer curve to the untreated condition (DOR = 0). The author may use estimated efficiencies of 10% and 80% for the case of DOR=1:50 and 1:25 during the fitting, respectively.
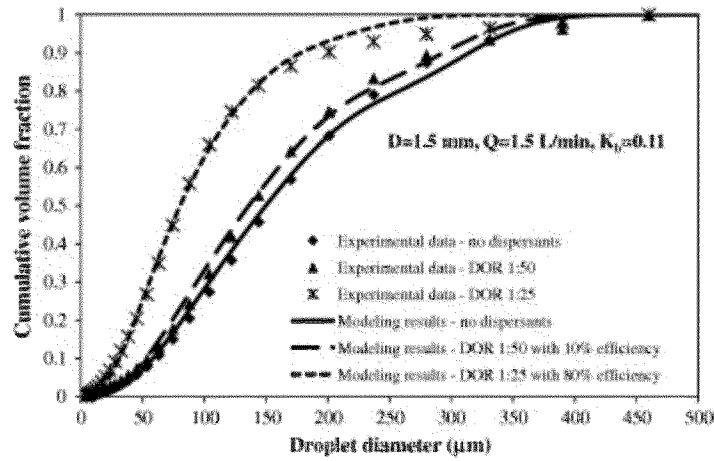
Figure 1: Comparison of oil droplet size distribution between VDROP-J and experimental data.

(*Source: Zhao et al. 2014*)

2.3 Modified Weber Number Approach

There is no validation conducted for the MEF and droplet breakup approaches for droplet size prediction with chemical dispersant application. However, chemical dispersion is one of the

iv

important technologies in offshore oil spill response, and promising in responding to deepwater release. Thus, an approach in predicting droplet size with chemical dispersant is desired.

Johansen et al. (2013) has proposed a modified Weber number approach for such purpose based on the conventional Weber number approach by Wang and Calabreses (1986). In Johansen et al. (2013), Weber number scaling law was used to fit their experimental data, expressed as:

$$d'/D = A \text{we}^{-3/5}$$
(9)

where d' is characteristic droplet diameter (m) D is the nozzle diameter (m), A id a factor of proportionality and $We = \rho U^2 D / \sigma$ is the Weber number; ρ is density of the liquid in the jet (oil) (kg/m^3) U is the exit velocity (m/s), and σ is the interfacial tension between oil and water (N/m or kg/s^2). However, this simple Weber scaling law only fit well on DOR=0, for other DOR experiments, this scaling law do not fit it. Based on these available data, a new prediction model (modified weber number) is used for oil droplet size distribution with and without chemical dispersant.

The modified Weber number, We^*, is defined as follows:

$$We^* = \frac{We}{1 + B Vi \left(d_{50}/D\right)^{1/3}}$$
(10)

where We is the Weber number, $Vi = We/Re$ is the viscosity number, d_{50} is the median droplet diameter (m), D is the nozzle size (m), B is an empirical coefficient determined by experimental analysis. The relative droplet size $d50/D$ can be expressed as:

$$\left(d_{50}/D\right) = A\left(We^*\right)^{-3/5}$$
(11)

where A is an empirical constant. Based on the data from Brandvik (2013) and Johansen et al. (2013) the value of A and B can be determined as A = 15.0 and B = 0.8.

Once d_{50} is determined, the droplet size distribution can be estimated using either lognormal or Rosin-Rammler distribution. Johansen et al. (2013) has concluded that Rosin-Rammler (Equation 12) distribution gives better fit of experimental data overall.

$$V(d) = 1 - \exp\left[-0.693\left(d/d_{50}\right)^{\alpha}\right]$$
(12)

where $V(d)$ is the cumulative distribution, and α is the spreading-parameter.

Although the mathematical formulations of three methods described above are of different level of complexity, all three methods require two or three tuning coefficients determined from regression. It seems that the efficiency and accuracy of droplet size prediction from these three methods are more or less the same. Comparatively, the complexity of the modified Weber number approach is lower than the other two, leading to advantage in real-world application. Therefore, the modified Weber number approach is selected in this study to fit the new experimental data with performance validation.

v

3 Prediction of Droplet Size Distribution

3.1 Experimental settings

A series of experiments of droplet size measurement for two types of oils (IFO-120 and ANS) have been conducted by the COOGER in BIO. The current flow rate for the experiments is set to 1 cm/s and the oil temperature is set to 80 °C. The detailed settings of the other parameters (i.e., oil amount, water temperature, injection time, and flow in the tank) are listed in Tables 1 and 2. 24 experiments were conducted for each types of oil by consideration of seasonal conditions (spring and summer). As shown in Tables 1 and 2, the experiment No.1 to 12 were set based on spring condition with slightly lower water temperature (mostly lower than 10°C) . In contrast, the experiments of No. 13 to 24 were set based on summer condition with warm water temperature (mostly higher than 10°C). The "R" marked in the experiment No. denoted a repeated experiment with slightly adjusted conditions (e.g., different DOR). In addition, some of the repeated experiments (i.e., 6R, 7R, 10R and 11R), which were scheduled in spring but not conducted due to abnormal weather conditions with rising water temperature, were actually conducted late fall.

There were four dispersant-oil ratios (0, 1:250, 1:100, and 1:25) for the spring condition. Comparatively, the settings of dispersant-oil ratios are slightly different from which in the spring condition, which are 1:200 and 1:20.

Table 1: Experimental settings for droplet size analysis for IFO-120

No.	Factors		Measurements					
	Oil	DOR	Date	Oil Amount (g)	Water Temperature (°C)	Injection Time (sec)	Flow in the Tank (gpm)	Injection Pressure (psi)
1	IFO-120	0	9-Jun-14	145.2	13.0	5	600	40
2	IFO-120	1:250	20-Jun-14	199.6	12.2	7	600	62
2R	IFO-120	1:200	04-Dec-14	208.2	6.7	7	600	60
3	IFO-120	1:100	20-Jun-14	213.9	13.2	7	600	62
4	IFO-120	1:25	11-Jun-14	179.1	12.8	9	600	40
4R	IFO-120	1:20	05-Dec-14	219.6	5.6	10	600	30
5	IFO-120	0	17-Jun-14	275.1	12.0	7	600	62
6R	IFO-120	1:200	04-Dec-14	215.6	6.6	8	600	60
7R	IFO-120	1:100	10-Dec-14	239.3	7.5	8	600	60
8	IFO-120	1:25	11-Jun-14	255.8	13.2	9	600	40
8R	IFO-120	1:20	05-Dec-14	243.3	5.4	10	600	60
9	IFO-120	0	17-Jun-14	359.6	12.7	7	600	62
10R	IFO-120	1:200	04-Dec-14	221.7	6.6	8	600	60
11R	IFO-120	1:100	17-Dec-14	N/A	4.9	10	600	60
12	IFO-120	1:25	16-Jun-14	354.8	12.5	9	600	62
12R	IFO-120	1:20	10-Dec-14	204.8	6.8	9	600	60
13	IFO-120	0	12-Sep-14	256.8	14.9	7	600	60
14	IFO-120	1:200	15-Sep-14	279	13.5	8	600	60
15	IFO-120	1:100	16-Sep-14	336.2	14.0	8	600	60
16	IFO-120	1:20	17-Sep-14	315.9	14.7	7	600	60

17	IFO-120	0	12-Sep-14	293.3	14.7	8	600	60
18	IFO-120	1:200	15-Sep-14	331.8	13.8	8	600	60
19	IFO-120	1:100	16-Sep-14	353.8	14.7	7	600	60
20	IFO-120	1:20	17-Sep-14	345.6	15.2	7	600	60
21	IFO-120	0	12-Sep-14	303.6	15.2	8	600	60
22	IFO-120	1:200	15-Sep-14	363.3	14.0	8	600	60
23	IFO-120	1:100	16-Sep-14	352.6	14.7	7	600	60
24	IFO-120	1:20	17-Sep-14	380	16.0	7	600	60

Note: R indicates repeated experiment.

Table 2: Experimental settings for droplet size analysis for ANS

No.	Factors		Measurements					
	Oil	DOR	Date	Oil Amount (g)	Water T (°C)	Injection Time (sec)	Flow in the Tank (gpm)	Injection pressure (psi)
1	ANS	0	22-May-14	208.0	11.4	4	600	40
2	ANS	1:250	23-May-14	280.0	10.6	5	600	40
2R*	ANS	1:200	02-Dec-14	290.5	6.4	5	600	40
3	ANS	1:100	23-May-14	284.5	11.2	5	600	40
4	ANS	1:25	26-May-14	283.0	8.4	5	600	40
4R	ANS	1:20	03-Dec-14	287.2	6.8	5	600	40
5	ANS	0	26-May-14	279.3	8.4	5	600	40
6	ANS	1:250	30-May-14	279.7	7.7	5	600	40
6R	ANS	1:200	02-Dec-14	335.0	6.1	5	600	40
7	ANS	1:100	30-May-14	276.3	8.5	5	600	40
8	ANS	1:25	02-Jun-14	277.4	9.4	5	600	40
8R	ANS	1:20	03-Dec-14	297.2	7.0	5	600	40
9	ANS	0	02-Jun-14	281.4	9.7	5	600	40
10	ANS	1:250	06-Jun-14	281.0	10.3	5	600	40
10R	ANS	1:200	17-Dec-14	344.5	5.4	5	600	40
11	ANS	1:100	06-Dec-14	276.8	10.7	5	600	40
12	ANS	1:25	09-Jun-14	280.6	12.5	5	600	40
12R	ANS	1:20	10-Dec-14	295.7	7.3	5	600	40
13	ANS	0	05-Sep-14	303.7	17.7	5	600	40
14	ANS	1:200	08-Sep-14	295.2	16.0	5	600	40
15R	ANS	1:100	10-Sep-14	304.3	13.8	5	600	40
16	ANS	1:20	10-Sep-14	291.9	14.7	5	600	40
17	ANS	0	05-Sep-14	299.6	18.1	5	600	40
18	ANS	1:200	08-Sep-14	297.7	16.2	5	600	40
19	ANS	1:100	09-Sep-14	283.4	15.3	5	600	40
20	ANS	1:20	11-Sep-14	289.6	14.1	5	600	40
21	ANS	0	08-Sep-14	297.1	15.1	5	600	40
22	ANS	1:200	09-Sep-14	281.8	14.2	5	600	40
23	ANS	1:100	10-Sep-14	284.4	13.4	5	600	40
24	ANS	1:20	11-Sep-14	285.8	13.6	5	600	40

| 25 | ANS | 1:50 | 11-Sep-14 | 316.2 | 17.6 | 6 | 600 | 40 |

Note: R indicates repeated experiment.

3.2 Measured Droplet Size Distributions

The droplet size distributions of IFO-120 based on different DOR and seasonal conditions are shown in Figures 2 to10. In addition, the droplet size distributions of ANS are listed in Figures 11 to 21. The ranges of DOR for the ANS experiment (Figures 11 to 20) were the same as which for the IFO-120. A series of experiments with DOR =1:50 are currently conducting by COOGER (one set of result is listed in Figure 21), further analysis will be conducted for this case.

As shown in Figure 2, the distribution and corresponding median of the droplet size distribution from experiment No. 1, 5, and 9 based on same type of oil (IFO-120), DOR = 0, seasonal condition (spring, similar water temperature) but different oil amount, injection time, and injection pressure. In addition, the first two experiments (No. 1 and 5) have the same peak diameter (d_p = 259 μm), but slightly different d_{50} (258 μm in No. 1 and 176 in No. 5). The third experiment showed smaller d_{50} (186 μm) and d_p (100 μm). This may be caused by relatively large plume or more smaller droplets caught by LISST.

In summer condition, the experiment 13 and 21 has same d_p (391 μm) and very similar d_{50} (263 μm in No. 13 and 264 in No. 21), while the experiment 17 has a slightly smaller d_{50} (192 μm) and d_p (293 μm) with similar settings from which in spring condition. However, the droplet size distributions form No. 13 and 21 are not completed due to the limited measuring window of the LISST. Thus, the data from these two experiments will not be included in the further analysis. Comparing results from summer and spring, the d_p and d_{50} from summer is relatively higher than which from spring. Since the only significant different setting from summer to spring is the water temperature, which may be another factor that affecting the oil droplet size.

The droplet size distributions with similar conditions but different DOR in spring are listed in Figures 4, 5, 7, and 9. By comparing the d_p and d_{50} in the experiments with different DOR, it indicates that the change of droplet size is relatively insignificant with DOR from 0 to 1:100 (Figures 2, 5, and 7). However, a significant decrease droplet size is observed with DOR increasing from 1:100 to 1:20. Therefore, there are may be a threshold of DOR dosage that significantly changes the effects of dispersant on droplet size.

The droplet size distributions with similar conditions but different DOR in summer are listed in Figures 6, 8, and 10. For the warm cases (14, 18, and 22), experiment No.18 showed strong effects of truncation due to the maximum diameter can be measured by LISST instrument was 500μm. Both experiments 14 and 22 have similar but slightly smaller d_{50} compared with untreated cases (No.13 and 21), but the d_p from warm water are much smaller. This indicates that dispersant started to play a role in this case but the effects are not very strong.

For the case of DOR=1:100 with spring condition, the shape of the distribution and calculated d_{50} and d_p in experiment No.3 are very similar to the untreated case and DOR=1:250 cases of experiment No.5 and No.2, and the dispersant did not show a strong effects on the droplet distribution (Figure 7). Similar as experiment No. 18, experiment No.7R also showed strong effects of truncation. For the summer condition cases (Figure 8), although d_{50} and d_p for experiment No.15 does not change significantly compared with DOR=1:200 cases (e.g. No.14), d50 from experiment No. 19 and 23 are much smaller and the overall oil concentration are much higher. This indicates high dispersant effectiveness.

For the case of DOR=1:25 (or 20) with spring condition (Experiment No. 4, 8, and 12), while the first experiment showed very low oil concentration compared with the other two experiments. The second and the third experiments repeated very well with much higher oil concentration and smaller d_p (128 μm for No. 8 and 104 μm for No. 12) and d_{50} (99 μm for No. 8 and 93 μm for No. 12) (Figure 9). Similar trends can be observed for the summer condition cases (Figure 10).

Compared the droplet size distributions from spring to summer conditions with same DOR, the droplet sizes from the results in summer experiment are significantly smaller than which in winter condition. The only known parameter that is different from the spring and summer condition with same DOR is the water temperature. Therefore, temperature may help facilitate the effect of dispersant on reduction the droplet size. In general, the results from the cases with spring and summer conditions indicate very high effectiveness of chemical dispersants.

Compared with the droplet sizes of IFO-120, the droplet sizes of ANS are significantly smaller. The droplet size distributions from three experiments (No. 1, 5 and 9) with untreated ANS in spring conditions are shown in Figure 11. The d_p (75 - 88 μm) and d_{50} (68 - 81 μm) are different but not significant in these three experiments. However, there is an abnormal peak observed in No. 5, which may due to unknown effects (further experiments and analyses shall be needed). The droplet sizes from the experiments with summer condition (No. 13, 17 and 21) (Figure 12) are similar (d_p = 104 - 128 μm d_{50} = 89 - 101 μm) and higher than which from experiments with spring condition.

For the case of DOR=1:250 with spring condition, three experiments (No. 2, 6 and 10) have been conducted (Figure 13). In addition, three repeated experiments (No. 2R, 6R and 10R) with DOR=1:200 have also been conducted (Figure 14). Experiment No. 2 shows two d_p in one distribution which may due to influences from environment, and thus is difficult to be analyzed. Nevertheless, the droplet size distributions from No. 6 and 10 are highly similar with same d_p (75 μm) and similar d_{50} (63 μm for No. 6 and 66 μm for No. 10). The repeated experiments with DOR=1:200 show similar situation, the shape of the distribution and calculated d_{50} and d_p are very similar between No. 2R and 6R; while the situation of No. 10R is similar to which of No. 2. Compared with the untreated case (d_p = 75 - 88 μm), the smaller d_p (< 75 μm) in DOR=1:200 (or 250) show the effect of dispersant on oil droplet distribution. The droplet size distributions from the experiments (14, 18, and 22) based on summer condition are highly similar with identical d_p (75 μm) and very close d_{50} (64 - 65 μm). Experiments with DOR=1:200 (or 250) have slightly smaller d_{50} (64 - 65 μm) compared with untreated cases (13, 17 and 21) (d_{50} = 68 - 81 μm), as well as the d_p (75 μm for DOR = 200 or 250 and 75 - 88 μm for DOR = 0). This indicates that the effect of dispersant on ANS is more significantly than which on IFO-120 with very insignificant change of droplet size from DOR = 0 to 1:200.

Three experiments have been conducted for DOR=1:100 with spring condition (Figure 16). The d_{50} (55 - 58 μm) in experiment No.3, 7 and 11 are smaller than the DOR=1:200 (or 250) cases (d_{50} = 64 - 65 μm) while d_p (75 μm) are same. For the summer condition cases (Figure 17), d_{50} and d_p for experiment No.15R does not change significantly compared with DOR=1:200 cases (e.g. No.14), while the ones from experiment 19 and 23 are relatively smaller.

For the case of DOR=1: 25 with spring condition, the d_p (12 μm) and d_{50} (3 - 10 μm) from corresponding experiments (No. 8 and 12) are significantly lower than which from the experiments with DOR=1: 200 and 1: 100; while data from experiment No.4 appears abnormal distribution and could not be analyzed (Figure 18). The situations from the repeated experiments (No. 4R, 8R, and 12R) with DOR = 1:20 (Figure 19) are very similar to the original one (DOR = 1:25). Furthermore, similar trends can be observed for the summer condition cases (Figure 20).

ix

Figure 21 is a trial experiment of DOR=1:50 which is done in the summer of 2015, which indicate the droplet size of ANS is steadily decrease with increase DOR. It should also be noted that the droplet size distributions are significantly different from the experiments with DOR = 1:20 or 25 to the others. This may be cause by over dose of chemical dispersant. The other peaks in the distributions (Figures 18, 19 and 20) may be caused by the over-dosed dispersant or the unknown background components that were affected by the dispersant.

In general, the chemical dispersant plays an importance role in reduce the droplet size of ANS no matter in spring or summer conditions. The effectiveness of dispersant in reducing droplet size is higher on ANS than which on IFO-120. There may be thresholds for the dose of chemical dispersant to some oils (e.g., IFO-120) but will need further experiments to analyze. There may also be over dose of dispersant to some oils (e.g., ANS) when the DOR is high, eventually affecting the droplet size distribution. Future experiment will also need for this particular issue.
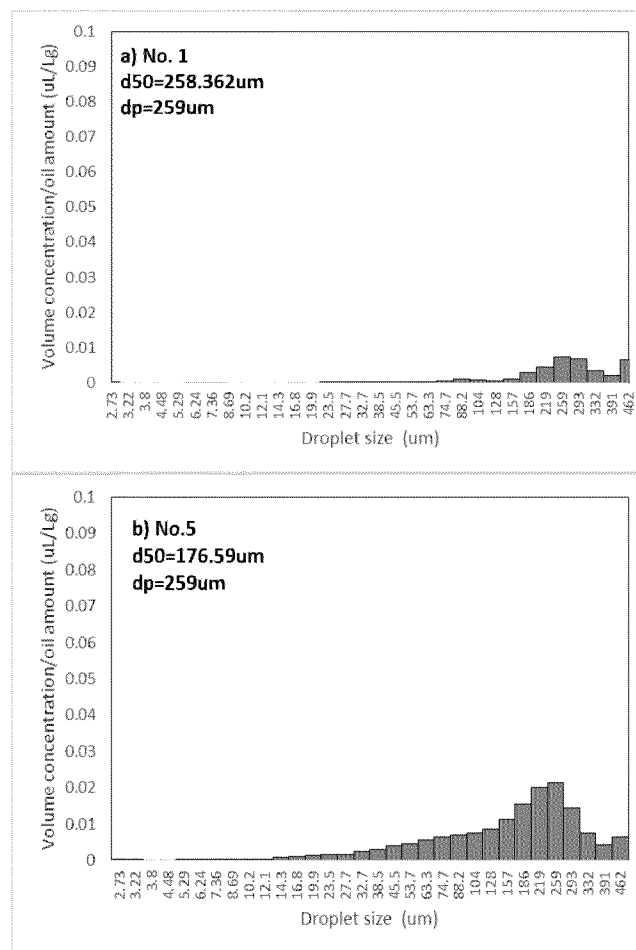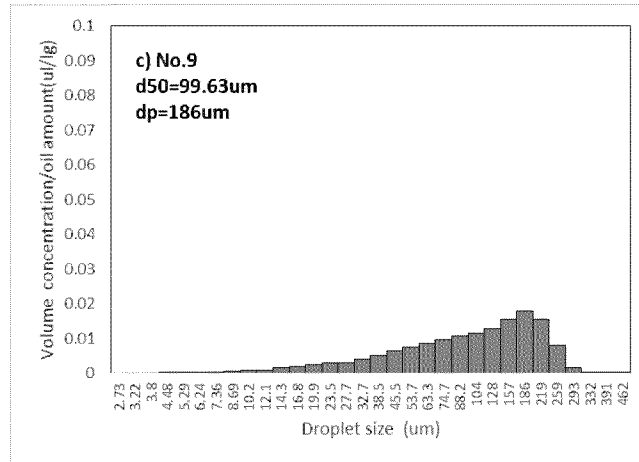
Figure 2: Experimental droplet size distribution of IFO-120 based on experiment a) No. 1, b) No. 5, and c) No.9 with DOR = 0 in spring condition
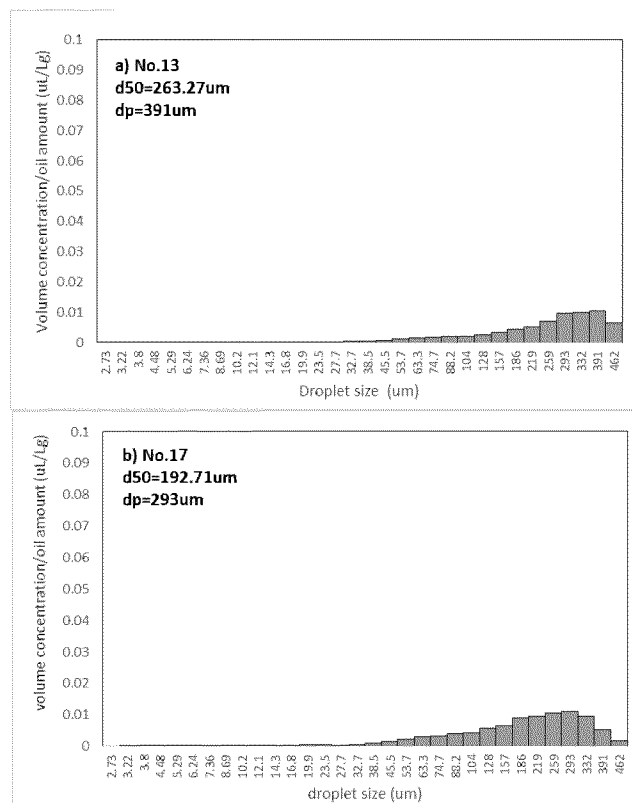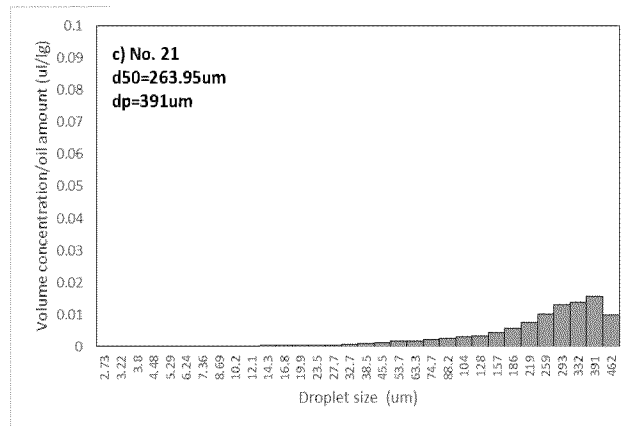
Figure 3: Experimental droplet size distribution of IFO-120 based on experiment a) No. 13, b) No. 17, and c) No. 21 with DOR = 0 in summer condition
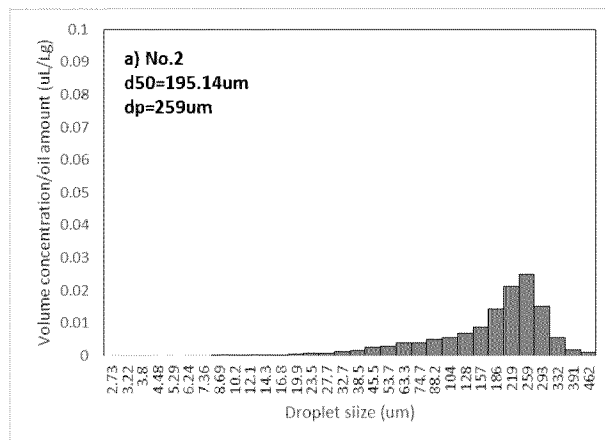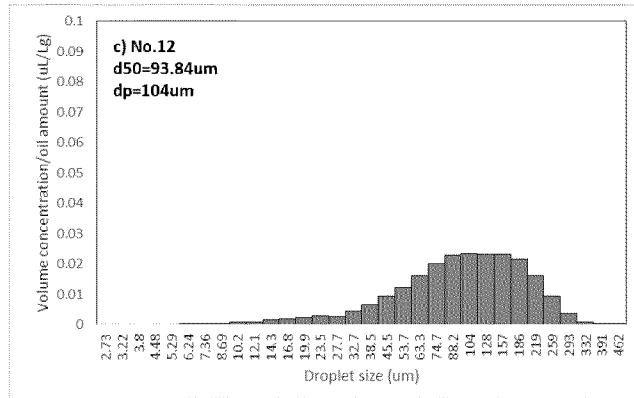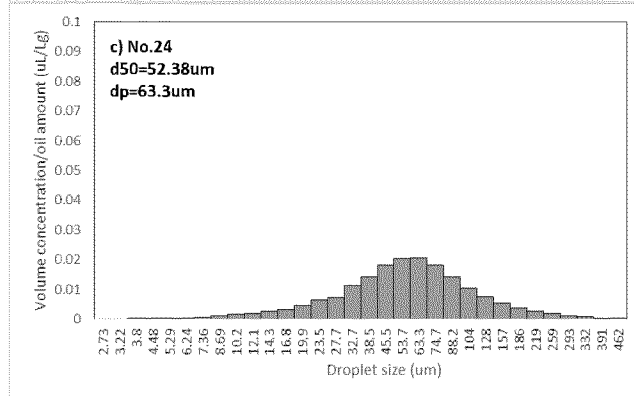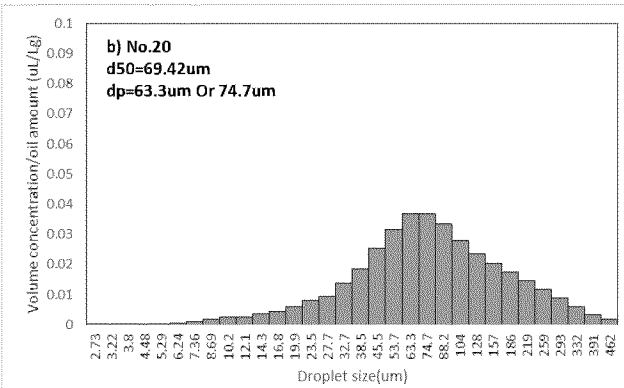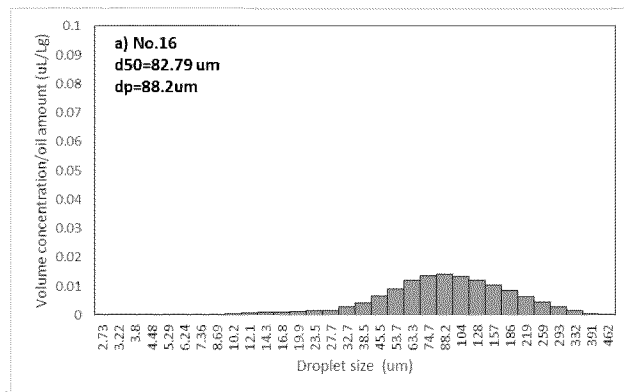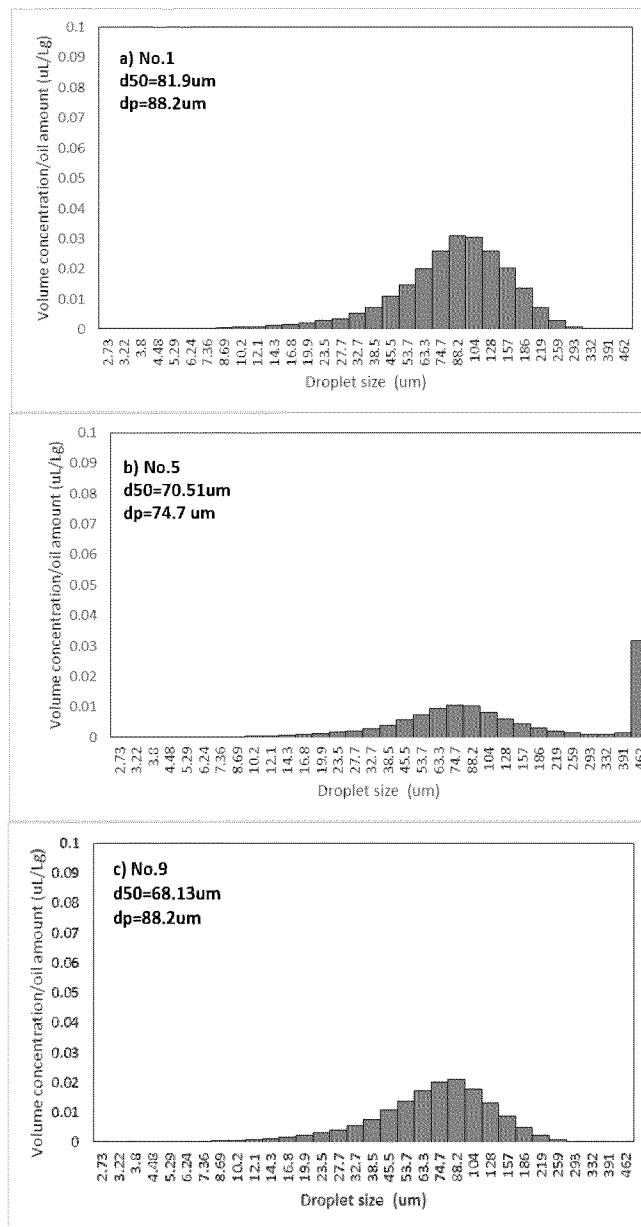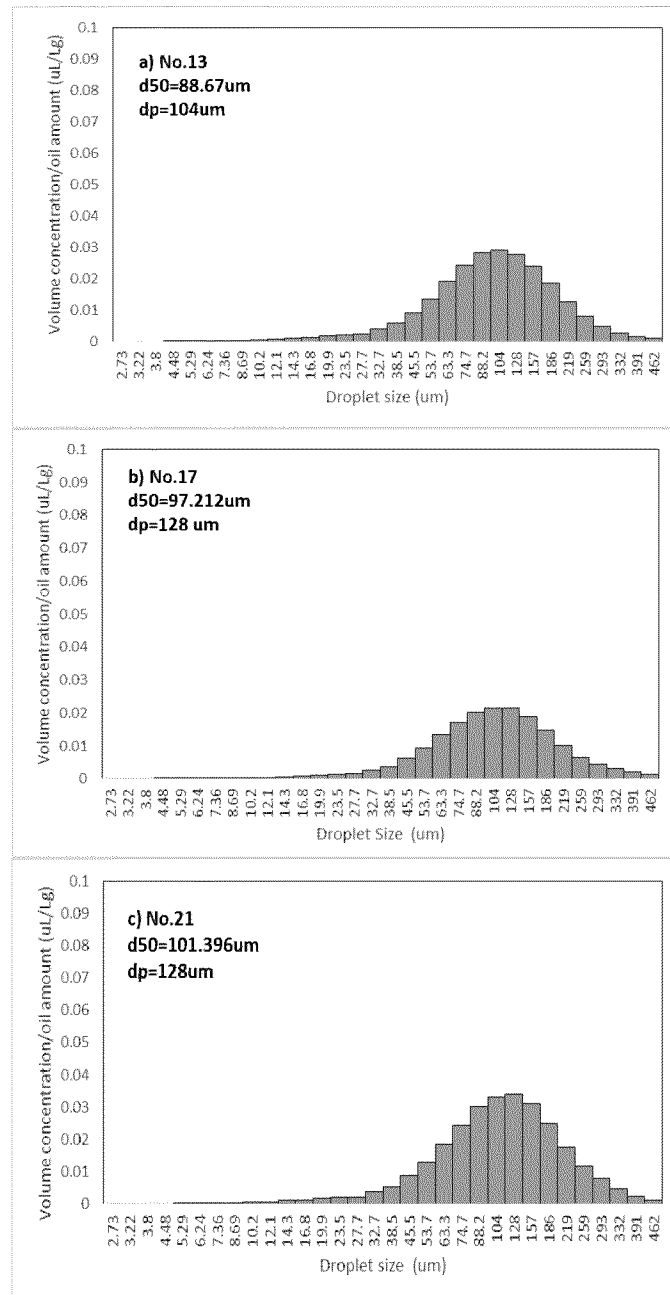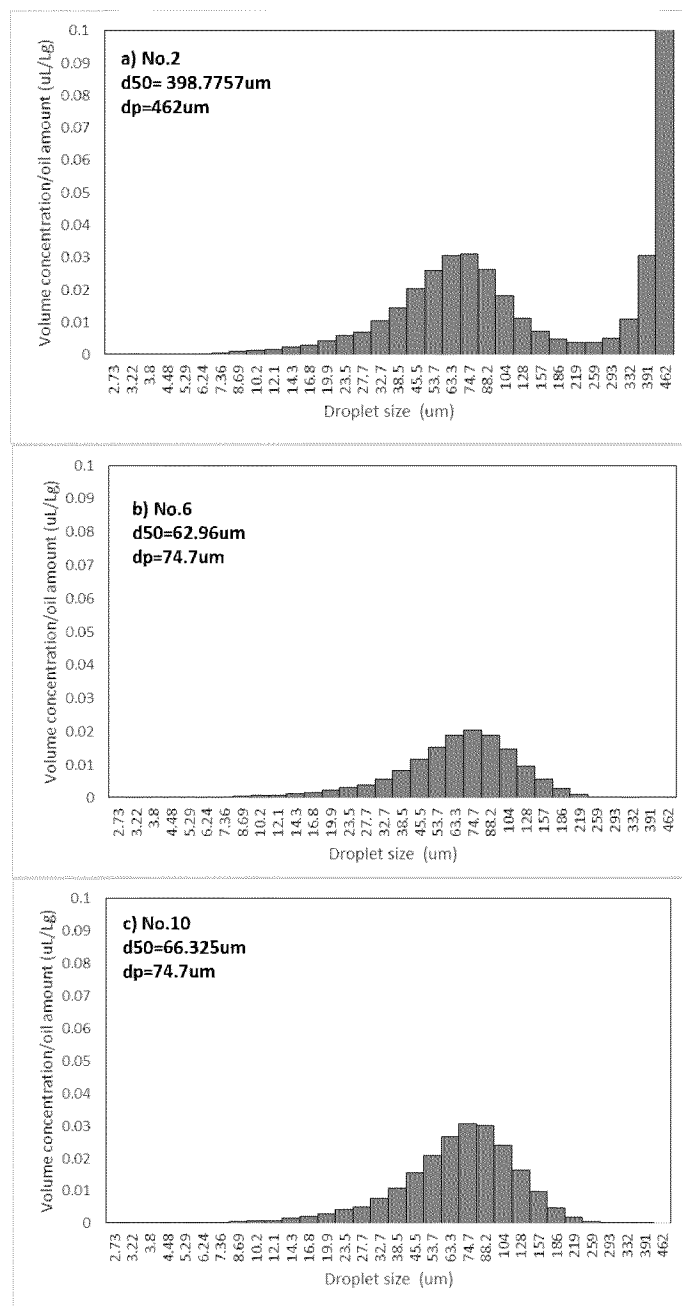

Figure 4: Experimental droplet size distribution of IFO-120 based on experiment a) No. 2 with DOR = 1: 250 in spring condition
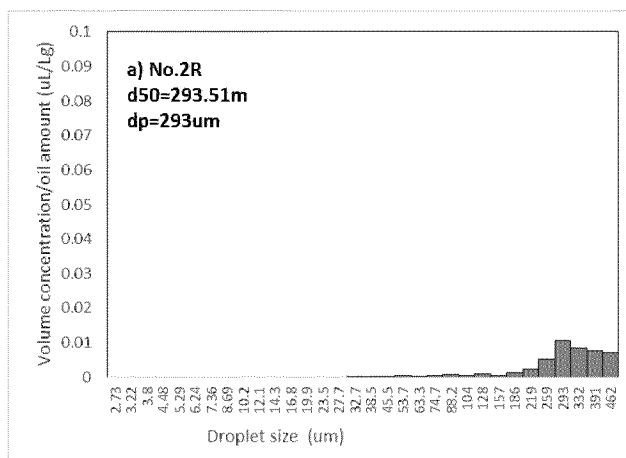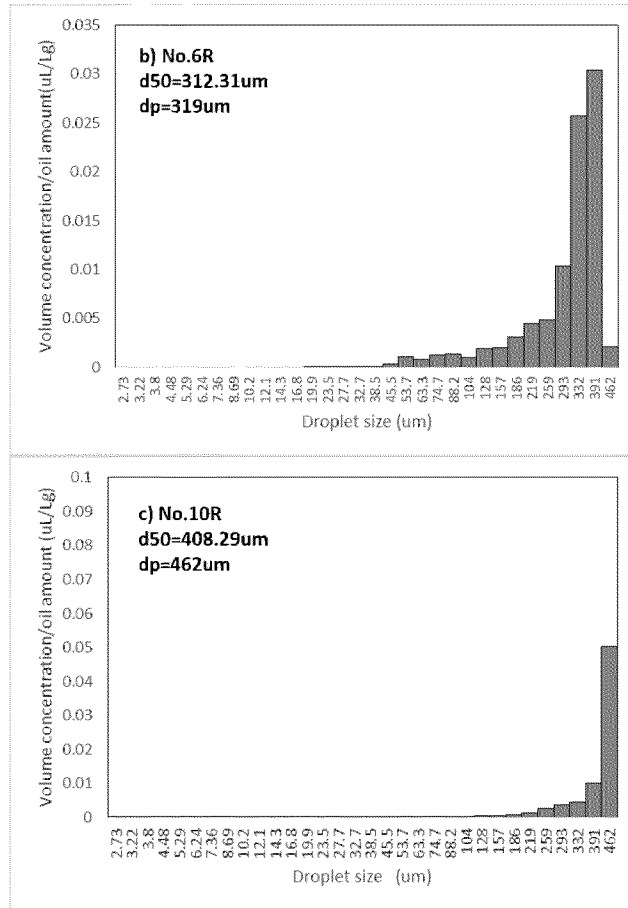
Figure 5: Experimental droplet size distribution of IFO-120 based on experiment a) No. 2R, b) No. 6R, and c) No.10R with DOR = 1: 200 in spring condition
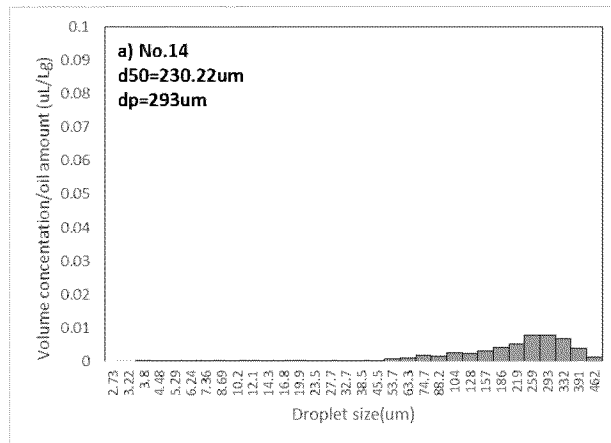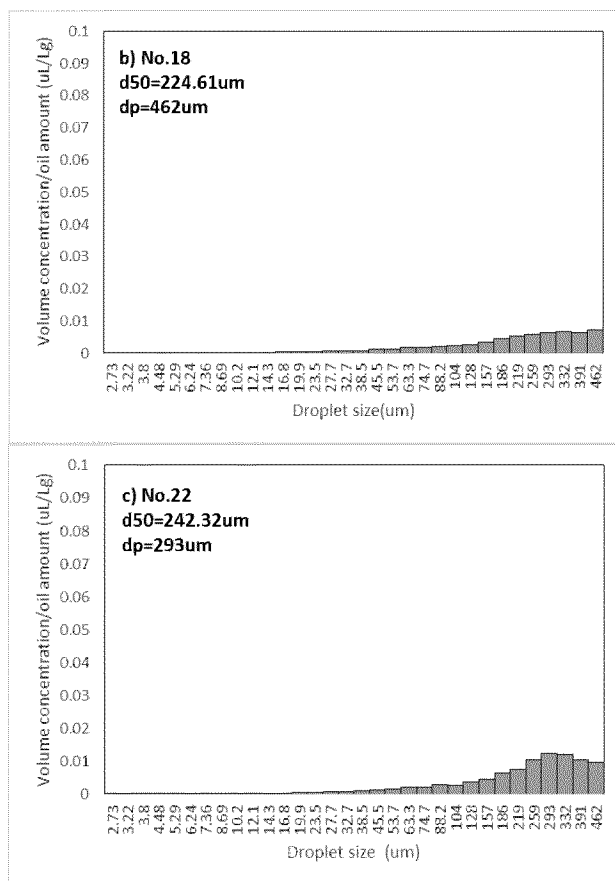
Figure 6: Experimental droplet size distribution of IFO-120 based on experiment a) No. 14, b) No. 18, and c) No. 22 with DOR = 1:200 in summer condition
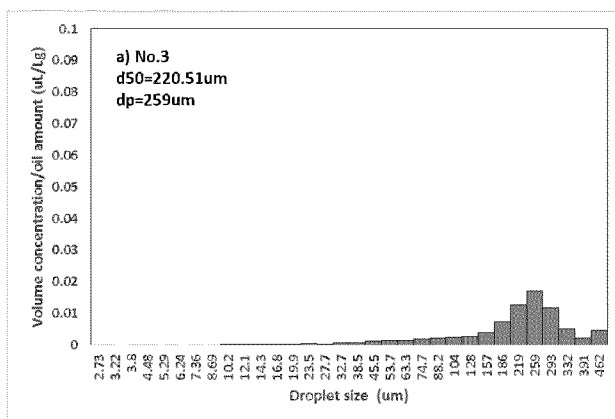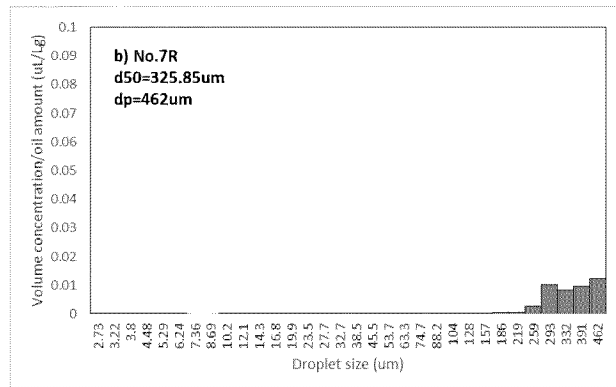
Figure 7: Experimental droplet size distribution of IFO-120 based on experiment a) No. 3, and b) No. 7, with DOR = 1:100 in spring condition
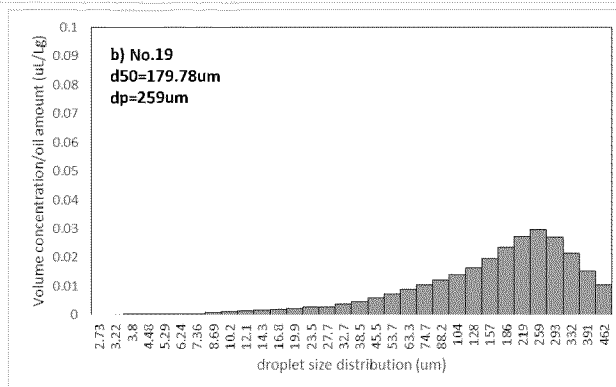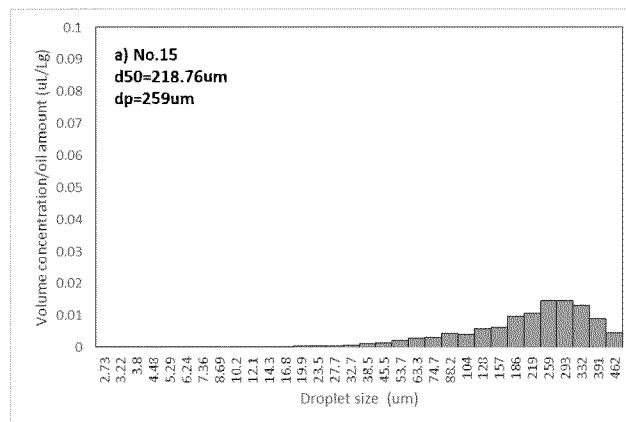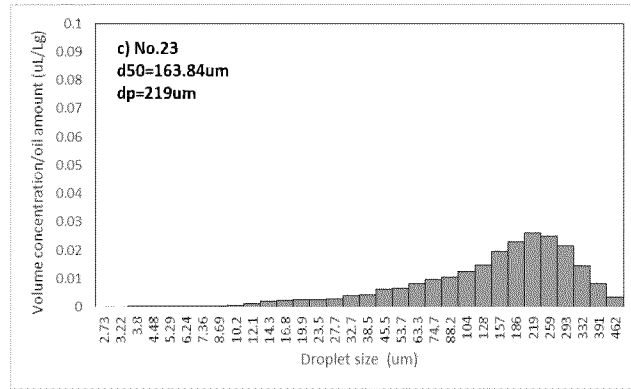
Figure 8: Experimental droplet size distribution of IFO-120 based on experiment a) No. 15, b) No. 19, and c) No.23 with DOR = 1:100 in summer condition
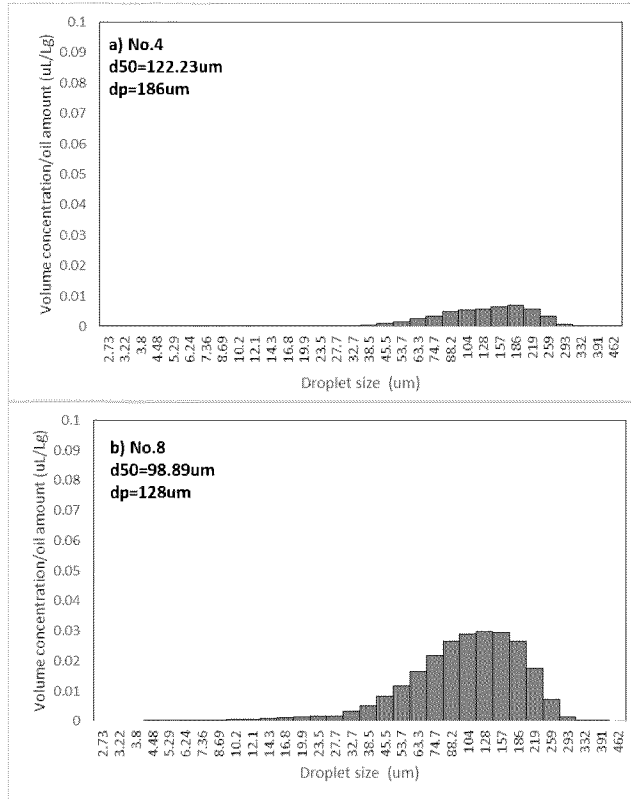
Figure 9: Experimental droplet size distribution of IFO-120 based on experiment a) No. 4, b) No. 8, and c) No.12 with DOR = 1:25 in spring condition
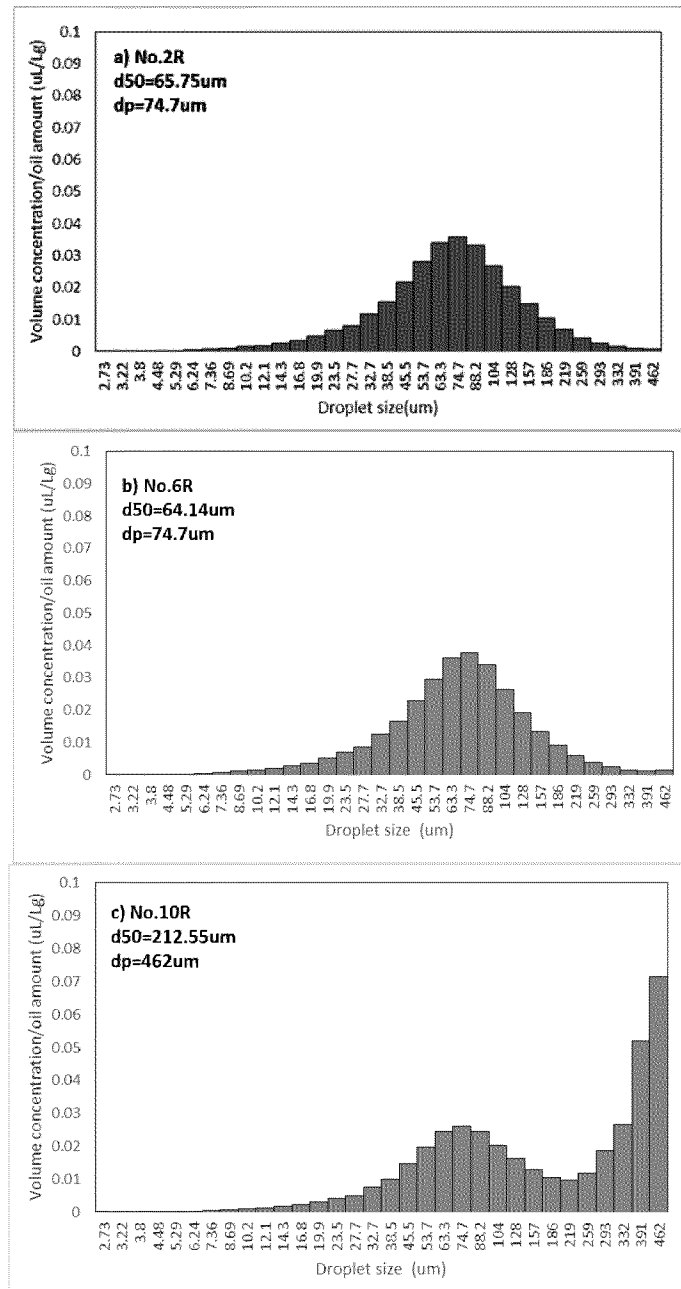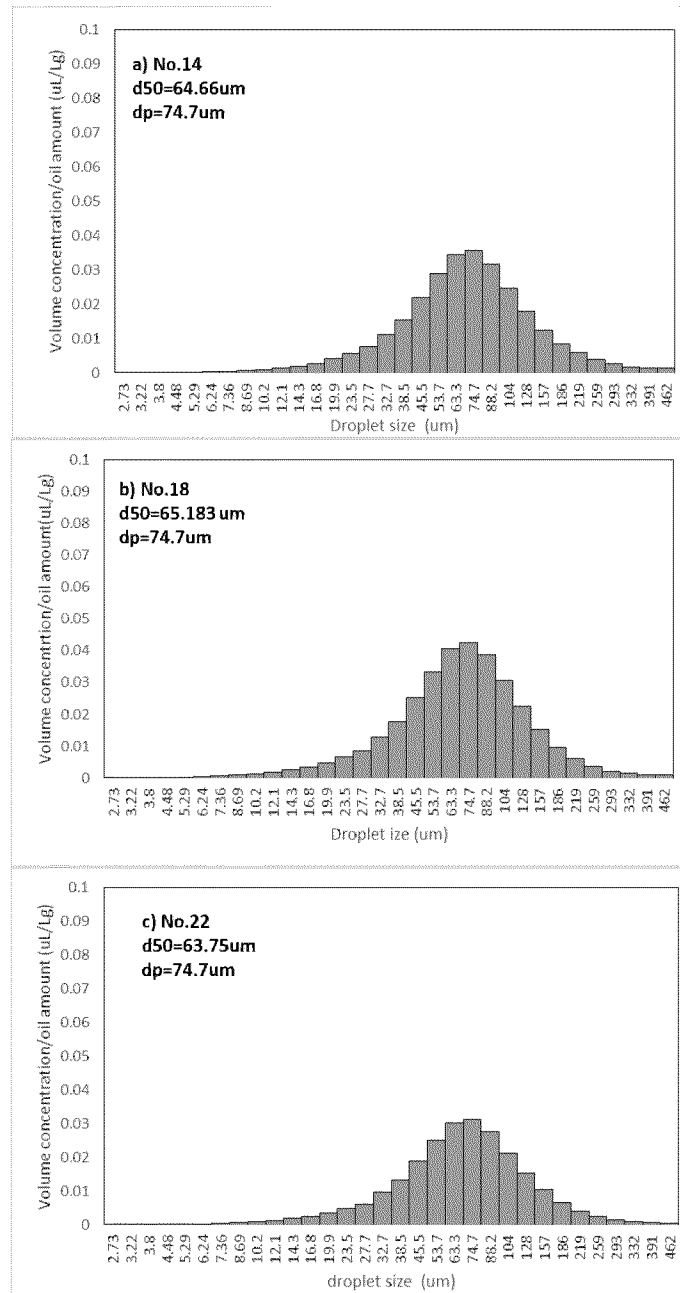
Figure 10: Experimental droplet size distribution of IFO-120 based on experiment a) No. 16, b) No. 20, and c) No.24 with DOR = 1:20 in summer condition

Figure 11: Experimental droplet size distribution of ANS based on experiment a) No. 1, b) No. 5, and c) No. 9 with DOR = 0 in spring condition

Figure 12: Experimental droplet size distribution of ANS based on experiment a) No. 13, b) No. 17, and c) No. 21 with DOR = 0 in summer condition
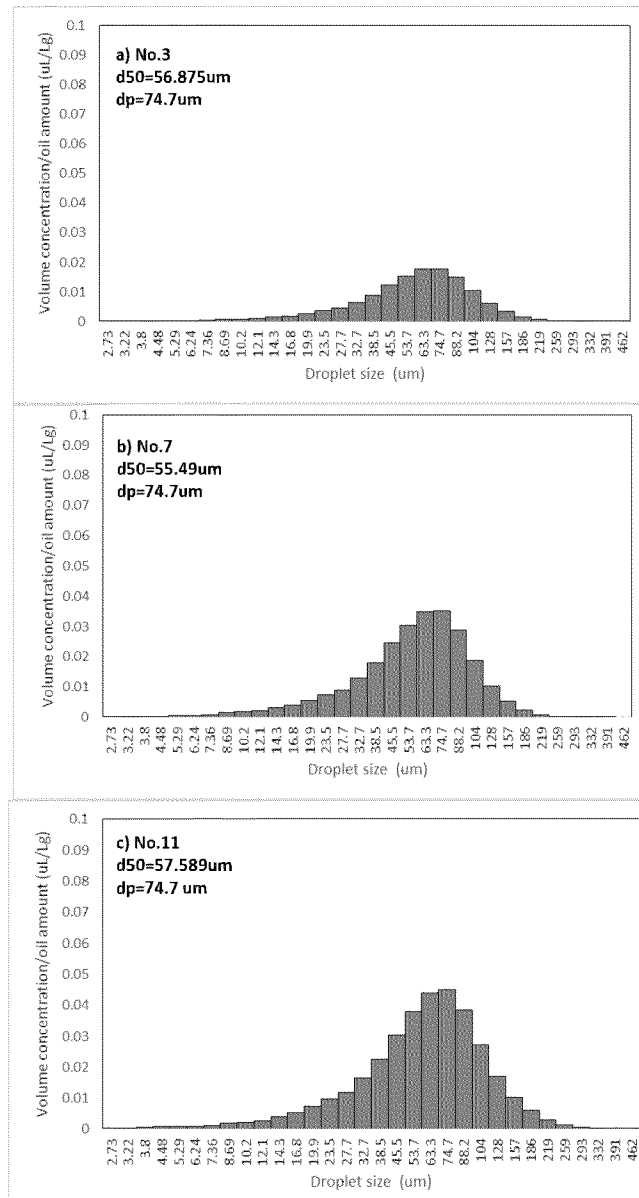
Figure 13: Experimental droplet size distribution of ANS based on experiment a) No. 2, b) No. 6, and c) No. 10 with DOR = 1:250 in spring condition
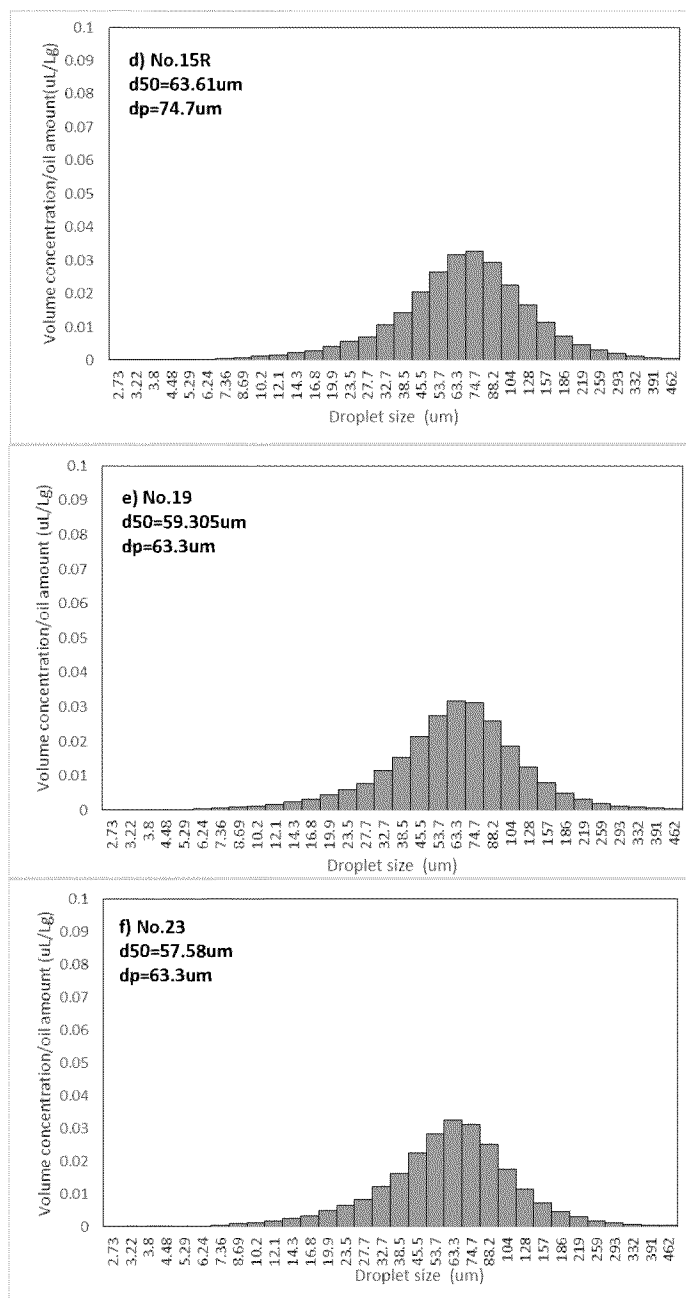
Figure 14: Experimental droplet size distribution of ANS based on experiment a) No. 2R, b) No. 6R, and c) No. 10R with DOR = 1:200 in spring condition

Figure 15: Experimental droplet size distribution of ANS based on experiment a) No. 14, b) No. 18, and c) No. 22 with DOR = 1:200 in summer condition

Figure 16: Experimental droplet size distribution of ANS based on experiment a) No. 3, b) No. 7, and c) No. 11 with DOR = 1:100 in spring condition

Figure 17: Experimental droplet size distribution of ANS based on experiment a) No. 15R, b) No. 19, and c) No. 23 with DOR = 1:100 in spring condition
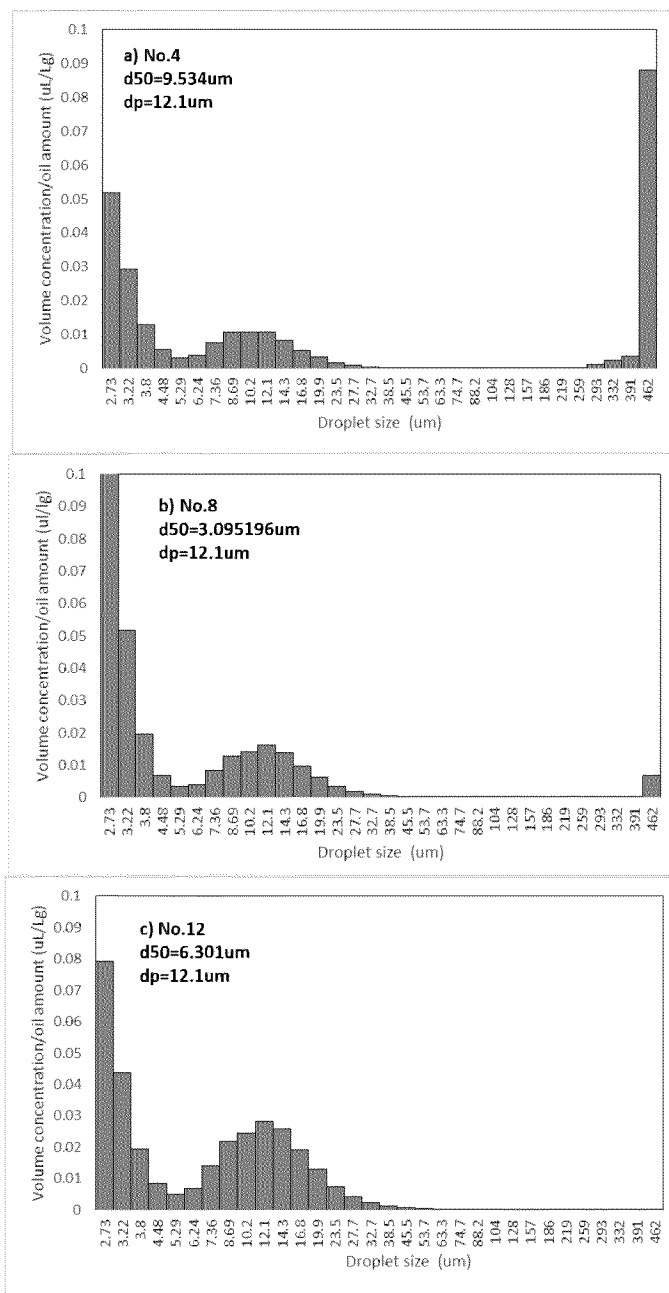
Figure 18: Experimental droplet size distribution of ANS based on experiment a) No. 4, b) No. 8, and c) No. 12 with DOR = 1:25 in spring condition
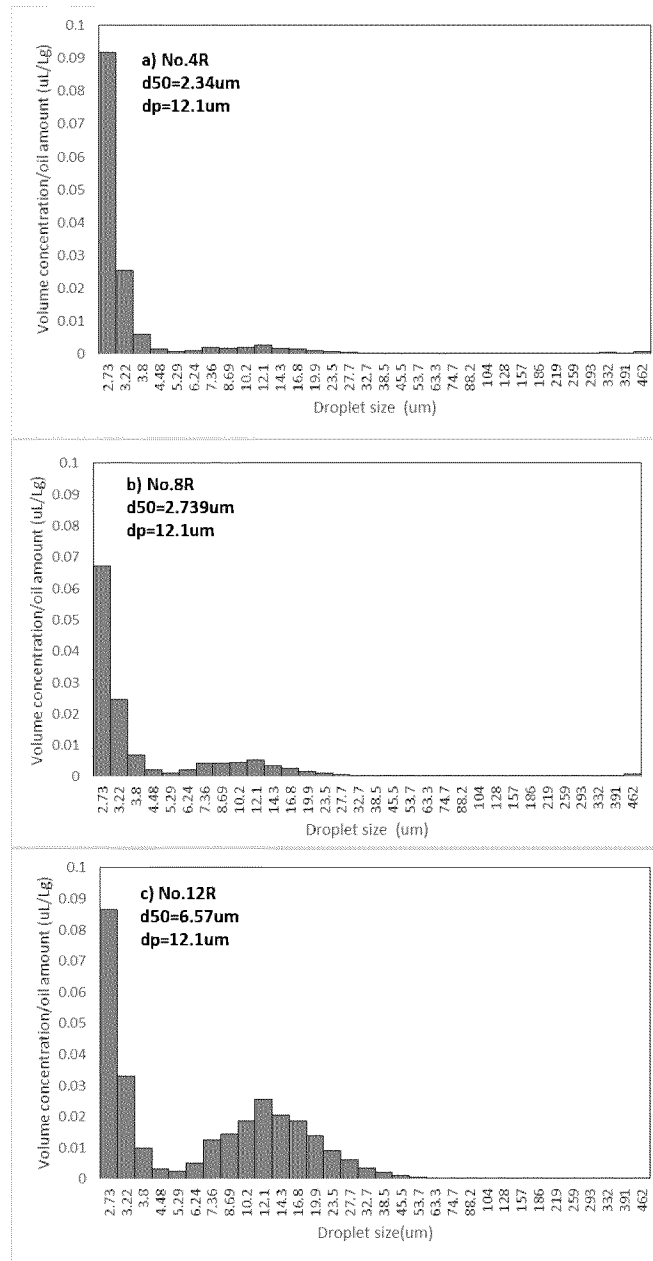
Figure 19: Experimental droplet size distribution of ANS based on experiment a) No. 4R, b) No. 8R, and c) No. 12R with DOR = 1:20 in spring condition
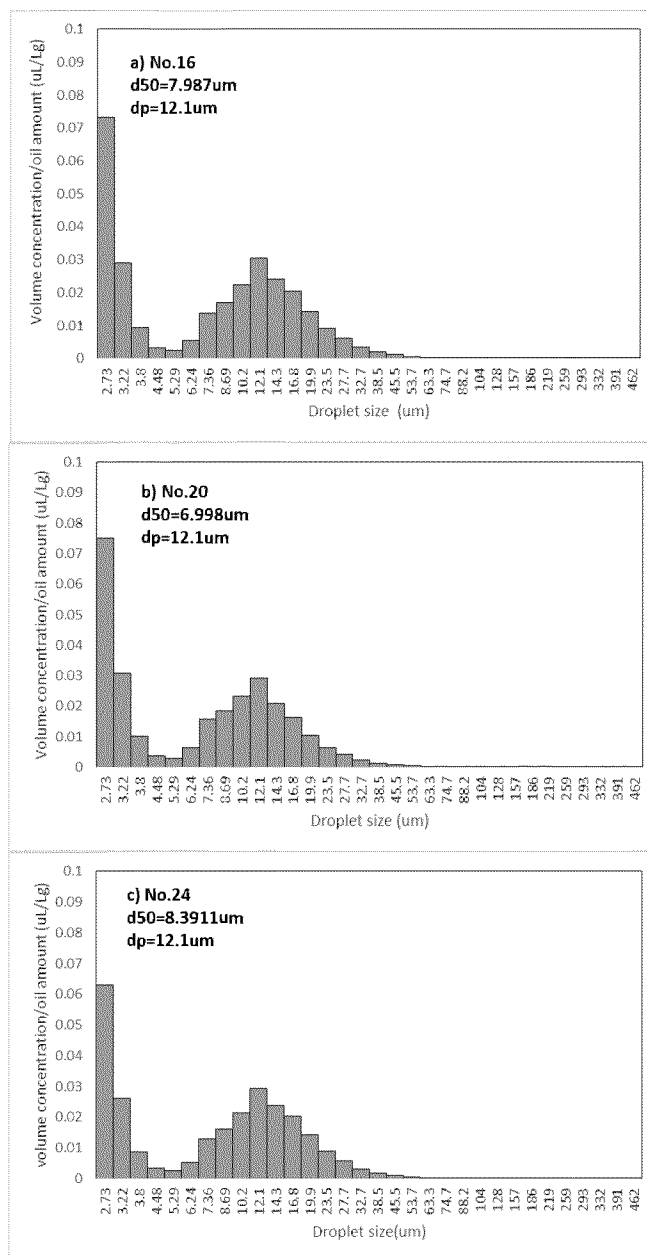
Figure 20: Experimental droplet size distribution of ANS based on experiment a) No. 16, b) No. 20, and c) No. 24 with DOR = 1:20 in Summer condition
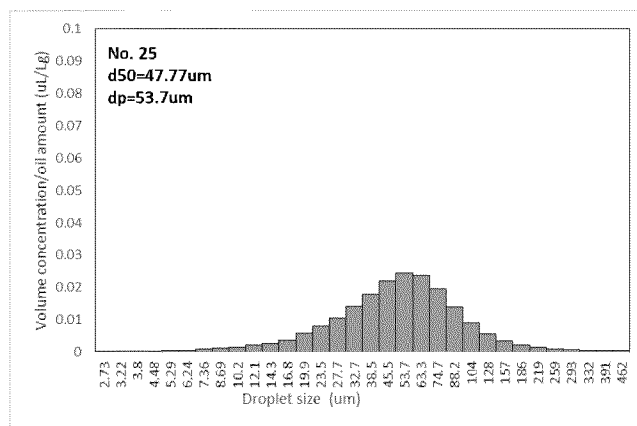
Figure 21: Experimental droplet size distribution of ANS based on experiment with DOR = 1:50 in summer condition

3.3 Data Fitting with Modified Weber Number Approach

Based on experimental settings (Table 1 and 2) and measured droplet size distributions (Figures 2 to 21), as well as the additional measurements on oil viscosity and IFT, the Weber number (We), Viscosity number (Vi) and Reynold number (Re) were calculated. The values of calculated and additional measured parameters for IFO-120 and ANS are listed in Tables 3 and 4. By normalize the d_{50} with the preset nozzle size in the experiments (D = 2.387 mm), the relationship between relative volume median droplet sizes (d_{50}/D) and modified Weber number (We* in Equation 11) for corresponding oils can be determined as in Figures 22 and 23. In comparison purpose, the corresponding data for Oseberg Blend based on the SINTEF tower tank experiments are also included in these figures.

As shown in Figure 22, for the treated IFO-120 crude oil with DOR ≤ 1:100, the modified Weber number approach fits the measured data IFO-120 well. The empirical constant A has been determined based on Equation 11 with regression approach. The empirical constant A for IFO-120 with DOR ≤ 1:100 is A = 5 which is significantly lower than the one for Oseberg Blend (A = 15, Johnsen et al., 2013). In the case of DOR > 1:100, the value of regressed constant is A = 2.54 for IFO-120 and A = 8.7 for Oseberg Blend. It indicates an about 45% of A values for both oils from DOR ≤ 1:100 to DOR > 1:100.

The regressions of constant A for ANS with different DOR conditions are listed in Figure 23. A reduction of 45% of A values is observed for ANS from DOR ≤ 1:100 to DOR > 1:100. It can be seen that the fitting situation for the regression of IFO-120 is better than which of ANS. Nevertheless, the trends of A with the change of DOR are consistent for IFO-120, ANS, and Oseberg Blend. Furthermore, the change of A values may be caused by the significant reduction of IFT. For the Oseberg Blend, when the DOR changed from 0 to 1:100 to 1:25, the corresponding IFTs were reduced from 15.5 to 0.5 to 0.09 mN/m (Johansen et al., 2013). However, the change of IFTs measured in the COOGER's experiments are from 46.78 (mN/m) to 56.97 (DOR=1:100), and 49.09 (1:20), which are much less significant than which from Johansen et al., 2013 If similar magnitude of reduction as Johansen et al. (2013) is applied to IFO-120, the two fitted line could get much closer. Therefore, besides the oil properties, measured IFT played a significant role in determining the values of empirical constant A and it must be examined further.

xxviii

xxix

Table 3: Data analyses for droplet size distribution of IFO-120

No.	Factors		Parameters								
	Oil	DOR	Q (L/min)	Viscosity (mPa·s)	d_{50} (μm)	dp (μm)	U (m/s)	IFT (mN/m)	We	Vi	Re
1	IFO-120	0	1.8063	44	230	259	5.6	46.78	$1.55×10^3$	5.27	293.5
1R	IFO-120	0									
2	IFO-120	1:250	1.7729	45	197.3	259	6.6	57.84	$1.74×10^3$	5.14	338.0
2R	IFO-120	1:200	1.849	45	293.510	293	6.887	57.84	$1.89×10^3$	5.36	352.556
3	IFO-120	1:100	1.8999	42	223.1	259	7.1	56.97	$2.02×10^3$	5.22	388.1
4*	IFO-120	1:25	1.2373	40	122.2	186	4.6	49.09	$9.96×10^2$	3.75	265.4
4R	IFO-120	1:20	1.365	40	195.310	462	5.058	49.09	$1.21×10^3$	4.14	292.84
5	IFO-120	0	2.4435	44	176.6	259	9.1	46.78	$4.08×10^3$	8.56	476.4
6R	IFO-120	1:200	1.676	45	312.310	319	6.241	57.84	$1.55×10^3$	4.86	319.451
7R	IFO-120	1:100	1.86	42	341.750	462	6.927	56.97	$1.94×10^3$	5.11	379.893
8	IFO-120	1:25	1.7672	40	98.9	128	6.6	49.09	$2.02×10^3$	5.36	379
8R	IFO-120	1:20	1.513	40	177.920	293	5.634	49.09	$1.49×10^3$	4.59	324.444
9	IFO-120	0	3.1941	44	100.4	186	11.9	46.78	$6.97×10^3$	11.19	622.7
10R	IFO-120	1:200	1.723	45	408.290	462	6.417	57.84	$1.64×10^3$	4.99	328.489
11R	IFO-120	1:100	N/A	42	370.340	462	N/A	56.97	N/A	N/A	N/A
12	IFO-120	1:25	2.4511	40	93.8	128	9.1	49.09	$3.91×10^3$	7.44	525.7
12R	IFO-120	1:20	1.415	40	211.340	293	5.27	49.09	$1.3×10^3$	4.29	303.449
13*	IFO-120	0	2.281	44	263.3	391	8.5	46.78	$3.13×10^3$	7.89	444.7
14	IFO-120	1:200	2.1684	45	230.2	259	8.1	57.84	$2.29×10^3$	6.28	413.4
15	IFO-120	1:100	2.613	42	215.2	259	9.7	56.97	$3.37×10^3$	7.17	533.7
16	IFO-120	1:20	2.8059	40	82.8	88.2	10.5	49.09	$4.51×10^3$	8.52	601.8
17	IFO-120	0	2.2795	44	192.7	293	8.5	46.78	$3.13×10^3$	7.99	444.5
18*	IFO-120	1:200	2.5788	45	224	462	9.6	57.84	$3.24×10^3$	7.47	491.6
19	IFO-120	1:100	3.1426	42	179.8	259	11.7	56.97	$4.88×10^3$	8.63	641.9
20	IFO-120	1:20	3.0697	40	69.38	74.7	11.4	49.09	$5.40×10^3$	9.32	658.4
21*	IFO-120	0	2.3596	44	254.6	391	8.8	46.78	$3.35×10^3$	8.27	460.1
22*	IFO-120	1:200	2.8236	45	245.9	293	10.5	57.84	$3.88×10^3$	8.18	538.3
23	IFO-120	1:100	3.1319	42	167.8	219	11.7	56.97	$4.85×10^3$	8.60	639.7

| 24 | IFO-120 | 1:20 | 3.3753 | 40 | 52.6 | 63.3 | 12.6 | 49.09 | 6.53×10^3 | 10.24 | 723.9 |

Table 4: Data analyses for droplet size distribution of ANS

No.	Factors		Parameters								
	Oil	DOR	Q (L/min)	Viscosity (mPa·s)	d_{50} (µm)	dp (µm)	U (m/s)	IFT (mN/m)	We	Vi	Re
1	ANS	0	3.617	7.2	81.9	88.2	13.471	63.97	5.84×10^3	1.52	3852.38
2*	ANS	1:250	3.895	8.2	398.780	462	14.507	60.52	7.16×10^3	1.97	3642.77
2R	ANS	1:200	4.041	8.2	65.750	74.7	15.051	60.52	7.71×10^3	2.04	3779.38
3	ANS	1:100	3.958	8.3	56.875	74.7	14.740	55.94	8.00×10^3	2.19	3656.72
4*	ANS	1:25	3.937	7.6	9.534	10.2	14.663	42.07	1.08×10^3	2.64	3972.47
4R	ANS	1:20	3.995	7.6	2.340	12.1	14.880	42.07	1.08×10^4	2.69	4031.43
5	ANS	0	3.885	7.2	70.512	74.7	14.471	63.97	6.74×10^3	1.63	4138.34
6*	ANS	1:250	3.891	8.2	62.961	74.7	14.492	60.52	7.14×10^3	1.96	3638.87
6R	ANS	1:200	4.66	8.2	64.140	74.7	17.357	60.52	1.02×10^4	2.35	4358.32
7	ANS	1:100	3.844	8.3	55.487	74.7	14.316	55.94	7.54×10^3	2.12	3551.38
8*	ANS	1:25	3.859	7.6	3.095	12.1	14.373	42.07	1.01×10^4	2.6	3893.87
8R	ANS	1:20	4.134	7.6	2.739	12.1	15.398	42.07	1.16×10^4	2.78	4171.8
9	ANS	0	3.915	7.2	68.131	88.2	14.580	63.97	6.84×10^3	1.64	4169.46
10*	ANS	1:250	3.909	8.2	66.325	74.7	14.559	60.52	7.21×10^3	1.97	3655.78
10R*	ANS	1:200	4.792	8.2	212.55	462	17.849	60.52	1.08×10^4	2.42	4481.91
11	ANS	1:100	3.851	8.3	57.589	74.7	14.341	55.94	7.57×10^3	2.13	355.76
12*	ANS	1:25	3.904	7.6	6.301	12.1	14.538	42.07	1.03×10^4	2.63	3938.78
12R	ANS	1:20	4.144	7.6	6.570	12.1	15.321	42.07	1.15×10^4	2.77	4150.74
13	ANS	0	4.225	7.2	88.870	104	15.735	63.97	7.97×10^3	1.77	4499.9
14	ANS	1:200	4.107	8.2	64.661	74.7	15.295	60.52	7.96×10^3	2.07	3840.5
15R	ANS	1:100	4.233	8.3	63.604	74.7	15.766	55.94	9.15×10^3	2.34	3911.2
16	ANS	1:20	4.061	7.6	7.987	12.1	15.124	42.07	1.12×10^4	2.73	4097.4
17	ANS	0	4.168	7.2	97.212	128	15.523	63.97	$7,76 \times 10^3$	1.75	4439.1
18	ANS	1:200	4.141	8.2	65.183	74.7	15.424	60.52	8.09×10^3	2.09	3873
19	ANS	1:100	3.942	8.3	59.305	63.3	14.683	55.94	7.94×10^3	2.18	3642.6
20	ANS	1:20	4.029	7.6	6.999	12.1	15.005	42.07	1.1×10^4	2.71	4065.1
21	ANS	0	4.133	7.2	101.396	128	15.393	63.97	7.63×10^3	1.73	4402.1

xxxii

22	ANS	1:200	3.920	8.2	63.747	74.7	14.600	60.52	7.25×10^3	1.98	3666.2
23	ANS	1:100	3.956	8.3	57.583	63.3	14.735	55.94	7.99×10^3	2.19	3655.4
24	ANS	1:20	3.976	7.6	8.391	12.1	14.808	42.07	1.07×10^4	2.68	4011.8

Note: * *mark means these data were not considered in the prediction of droplet size distribution due to incomplete measured distribution.*
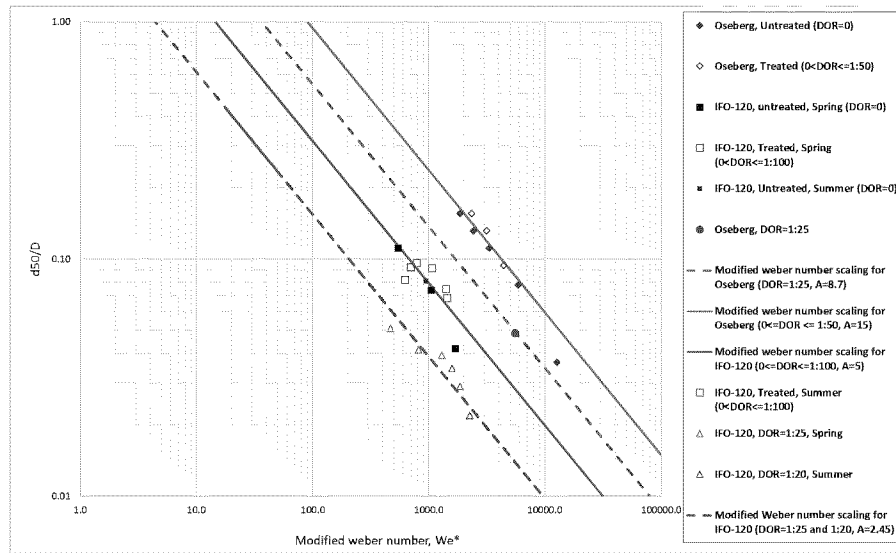
Figure 22: Data regression for constant A from modified Weber number and d_{50}/D for IFO-120
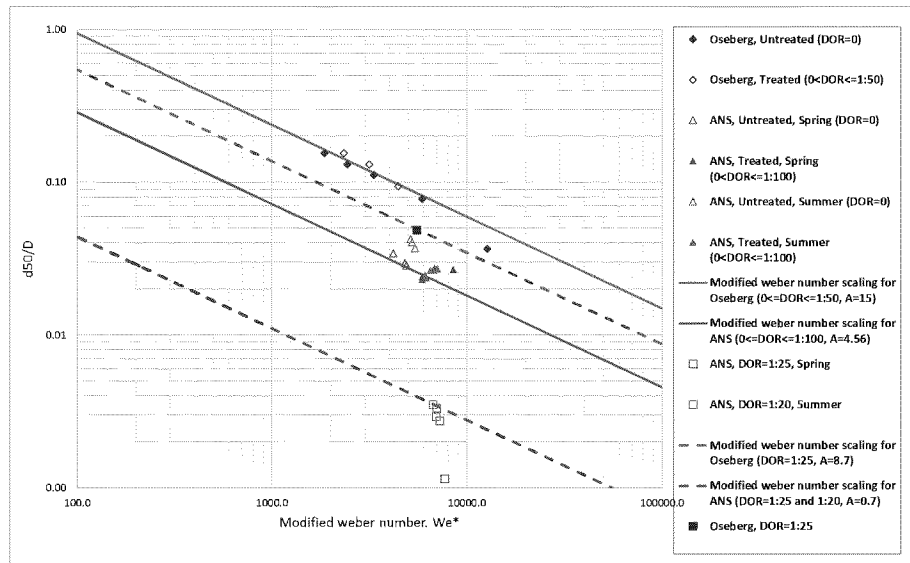
Figure 23: Data regression for constant A from modified Weber number and d_{50}/D for ANS

3.4 IFT and Reynolds Number Scaling

Due fact that the effects of oil/dispersant in water concentration affects IFT and in situ sampling may be impractical, as suggested by Johansen et al. (2013), some method for prediction of IFT related to a given DOR will be useful. IFT measurements with a variety of oils premixed with different dosages of dispersants might help to establish such relationships in more general terms. As demonstrated by MacKay and Hossain (1982), with same amount of oil and dispersant, the water volume affects the IFT significantly. In the direct sampling methods, the amount of oil/dispersant in 1L of sample from different experiments could vary significantly and therefore affects the IFT measurements. For example for Murban oil with DOR=1:1333, the IFT was 3.7 and 7.9 (mN/m) for 100 and 800 mL of water, respectively. Brandvik et al. (2013) provide a more advantage method for more consistent IFT measurement compared with the direct sampling methods. In this method, oil/water samples were collected at 1.5 m height above the nozzle in 1 L long necked measuring flask. Oil appeared as droplets in the water with size distribution depending on the DOR and method of dispersant application. The surface oil layer in the narrow neck of the bottle and was collected for IFT measurements after 24 h. using spinning drop method as described by Khelifa and So (2009), the Dataphysics Spinning Drop Tensiometer SVT-20N with control and calculation software SVTS 20 IFT was used. The IFT in this study were measured using a different method by premix 10 mg oil-dispersant in 100 mL seawater.

Before such a relationship is establish, we believe that the use of IFT should be avoided and the use of Modified Weber number approach should be re-considered. Wang and Calabrese (1986) have found that droplet breakup was governed by the Weber number scaling for small viscosity numbers ($Vi \rightarrow 0$), but that a Reynolds number scaling would apply for large viscosity number ($Vi \gg 1$):

$$\left(d_{50}/D\right) = C\left(\mathrm{Re}\right)^{-3/4}$$

(13)

where $C = A^{5/4}B^{3/4}$, and the Re is the Reynolds number given by

$$\mathrm{Re} = \frac{\rho U D}{\mu}$$

(14)

where ρ is the density of oil, U is the exit velocity, D is the nozzle diameter, and μ is the dynamic viscosity. Using of Reynolds scaling instead of modified Weber number scaling have the apparent advantage of avoiding the inconsistency IFT measurements and can make comparison of data from different sources easier.

The application of this concept for existing experimental data has been shown in Figure 24. The calculated and observed d_{50}/D correlates very well. In addition, the volume median diameters for IFO-120 are plotted against Reynolds number in Figure 25 together with data for Oseberg Blend by Brandvik et al. (2013). It can be seen from the plot that Reynolds scaling fits the data well. Values of empirical constants A were obtained for all IFO-120 combined (exclude DOR=1:25 (or 20)) and Oseberg Blend through regression analysis. A was 6.1 for combined data while the A for Oseberg Blend is 16.8. The data has shown that with the d50/D is slightly bigger (higher A) for summer condition cases than winter condition cases with same Reynolds number (Figure 25). The cases for ANS show quite difference compared with IFO-120 cases. The

DOR=0 and ≤1:100 experimental data points are more closed to Oseberg Blend data, the A for combined data of ANS (excluded DOR=1:25 (or 20)) is 10.5 (Figure 26). It is unclear if this is associated with uncertainties due to limited experimental data points or it is actually due to the effects of different water temperature. With more experimental data available, this observation will be revisited. Without considering the effects of temperature, the difference in A between IFO-120 and Oseberg Blend are considered to be the effects of oil type.

Furthermore, A has been reduced from 16.8 to 8.7 (49% reduction) for Oseberg, from 6.1 to 3.21 (47% reduction) for IFO-120 and 10.5 to 1.75 (83% reduction) for ANS (Figures 24 and 25). This is reduction can be used to model the effects of chemical dispersant on droplet size. Based on the experimental data on the three oils, it is proposed that a constant value A could be selected for Reynolds number scaling depending on oil types for cases of DOR ≤ 1:100. For DOR of 1:25, a 50% reduction of A may be used and a linear interpolation may be used to estimate A values for other DOR greater than 1:100 but less than 1:25 for Oseberg Blend and IFO-120. However, the change A values for ANS does not follow the linear relation. Data points of DOR = 1:50 for ANS is close to the one of DOR = 1:100 but relatively far from which of DOR=1:25 (or 20). This may be caused by the effects of oil type and further interpolations for the relation of DOR and A value for ANS will be needed in future study.
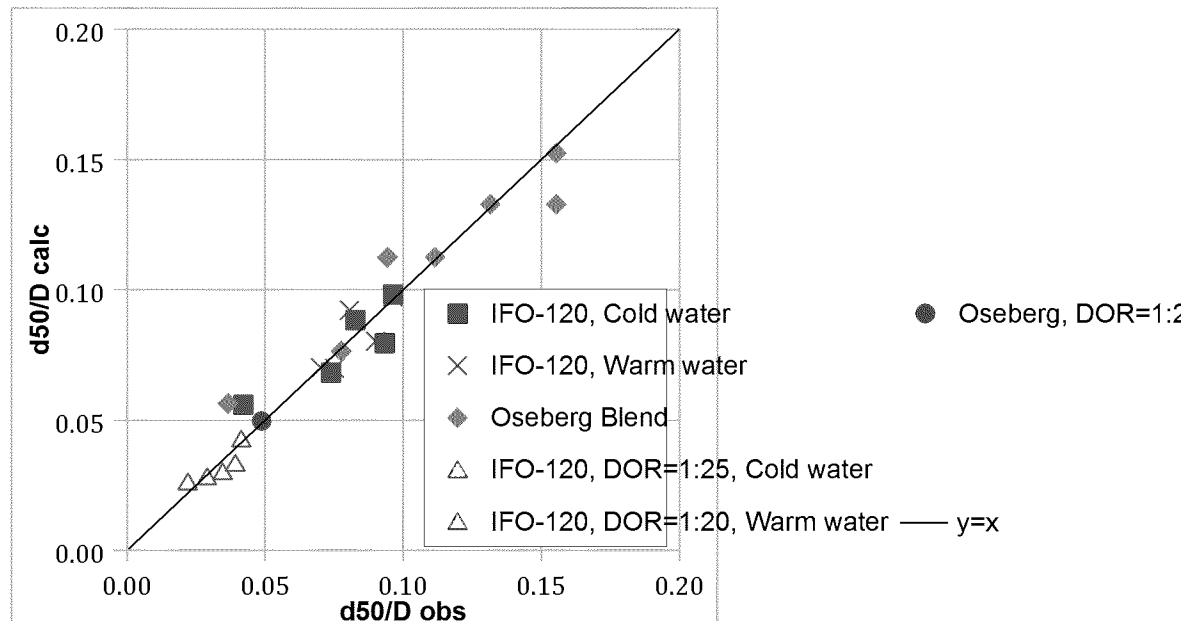
Figure 24: Measured (obs) and computed (calc) relative droplet sizes d50/D from experiments with IFO-120 and Oseberg Blend
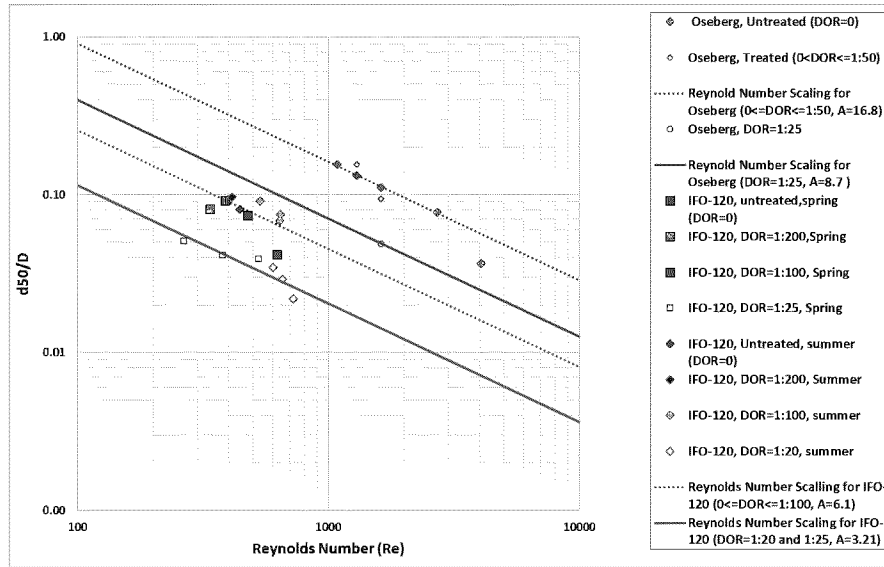
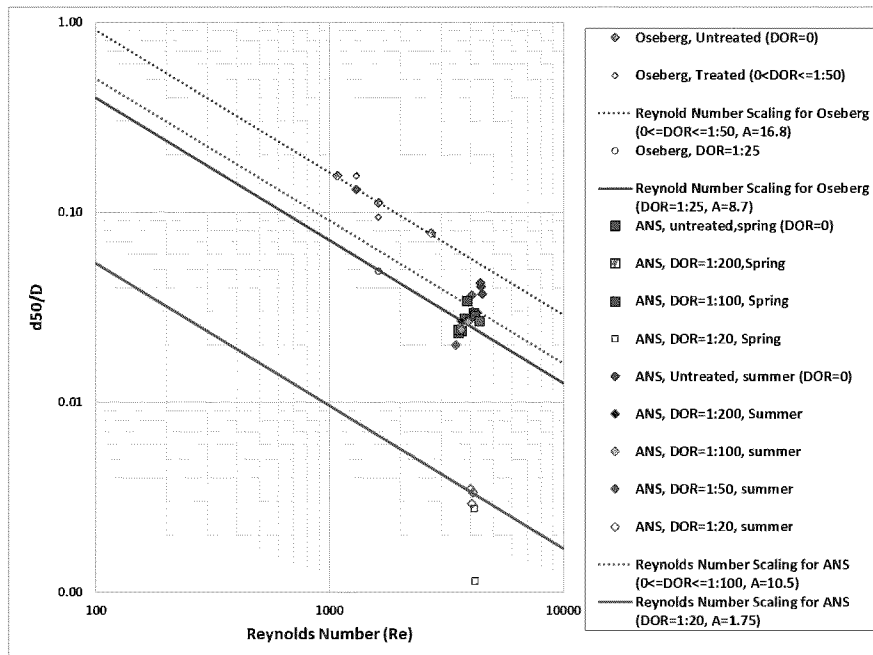**Figure 25:** Data regression for constant A from Reynolds number and d_{50}/D for IFO-120

Figure 26: Data regression for constant A from Reynolds number and d_{50}/D for ANS

3.5 Determination of Distribution Shape using Two-Step Rosin-Rammler Method

The sections above described how to predict the characteristic diameter, d_{50}, for different types of oils (i.e., IFO-120 and ANS). Correspondingly, further prediction of the statistical distribution for the droplet sizes around the characteristic diameter will be conducted in this section. According to Lefebvre (1989), two most commonly used distribution are lognormal and Rosin-Rammler distributions. Johansen et al. (2013) has also concluded that there is currently no theoretical basis for choosing the right distribution function and the choice of function must be

based on empirical data.

Johansen et al. (2013) have found that Rosin-Rammler could provide better overall fit of the experiment data and they have derived a spreading coefficient $\alpha = 1.8$ for the corresponding distribution. In this study, Rosin-Rammler distribution was also selected and corresponding regression analysis has been conducted to calculate the best spreading coefficients (Tables 5 and 6).

The initial data analysis has indicated that the distributions of the data with $d/d_{50} <= 1$ and $d/d_{50} > 1$ are significantly varied. Thus, it would be difficult and/or inaccurate to predict the measured IFO-120 and ANS data by only a single distribution.

In order to address this challenge, a two-step Rosin-Rammler approach was introduced by advancing from the Rosin-Rammler approach proved by Johansen et al. (2013). The proposed approach uses two separate spreading coefficients: α_1 for $d/d_{50} <= 1$ and α_2 for $d/d_{50} > 1$, providing better fit of the data in all cases. The data distribution and the corresponding regression results are shown in Figures 27 to 42. Regressed based on the single Rosin-Rammler distribution, the overall spreading coefficient (α) for IFO-120 is 2.33 which is larger than that for Oseberg Blend (1.8). For ANS, $\alpha = 1.77$, is smaller than which for Oseberg Blend ($\alpha = 1.8$). According to the two-step Rosin-Rammler approach, the average α_1 for IFO-120 is 2.01 and α_2 is 2.74. In addition, the average α_1 for ANS is 1.78 and α_2 is 1.63. Furthermore, the regression coefficients (R^2) for the regressions based on single and two-step Rosin-Rammler distributions were also calculated for both IFO-120 and ANS under different DOR and seasonal conditions (Figures 27 to 42). The R^2 for two-step Rosin-Rammler are higher than which for the single one in most of the case, indicating the advantage of the proposed two-step Rosin-Rammler approach.

Table 5: Spreading coefficient for Rosin-Rammler distribution of IFO-120

			All Data			Average		
			Single	2-step		Single	2-step	
			α	α_1	α_2	α	α_1	α_2
Summer	Untreated	No.13[*]	/	/	/			
		No.17	1.86	1.53	2.20			
		No.21[*]	/	/	/	1.86	1.53	2.20
	1:20	No.16	1.75	2.13	1.44			
		No.20	1.55	1.95	1.18			
		No.24	1.85	2..05	1.50	1.72	2.04	1.37
	1:100	No.15	1.96	1.50	2.54			
		No.19	1.57	1.30	2.00			
		No.23	1.59	1.31	1.975	1.71	1.37	2.17
	1:200	No.14	2.39	1.85	3.10			
		No.18[*]	/	/	/			
		No.22[*]	/	/	/			

1

Spring	Untreated	No.1*	/	/	/	2.39	1.85	3.10
		No.5	1.66	1.32	2.14			
		No.9	1.54	1.49	1.632	1.60	1.41	1.89
	1:25	No.4	2.13	2.24	2.10			
		No.8	2.05	2.31	1.83			
		No.12	1.77	1.99	1.62	1.98	2.18	1.85
	1:100	No.3	2.61	1.98	3.31			
		No.7R*	/	/	/			
		No.11R*	/	/	/	2.61	1.98	3.31
	1:250	No.2	2.39	1.72	3.20			
		No.6R*	/	/	/			
		No.10R*	/	/	/	2.39	1.72	3.20
Average						2.33	2.01	2.74

Note: "/" indicates that the data is unavailable due to incomplete droplet size distribution from measurement

Table 6: Spreading coefficient for Rosin-Rammler distribution of ANS

			All Data			Average		
			Single α	2-Step:		Single	2-step	
			α	α_1	α_2	α	α_1	α_2
summer	Untreated	No. 13	1.93	2.32	1.57			
		No. 17	1.87	2.29	1.51			
		No. 21	1.9	2.3	1.58	1.90	2.30	1.55
	1:20	No. 16	1.12	0.62	1.39			
		No. 20	1.12	0.61	1.34			
		No. 24	1.17	0.68	1.49	1.14	0.64	1.41
	1:100	No. 15R	1.99	2.24	1.65			
		No. 19	2.05	2.24	1.67			
		No. 23	2.03	2.20	1.66	2.02	2.23	1.66
	1:200	No. 14	1.96	2.26	1.49			
		No. 18	2.03	2.29	1.61			
		No. 22	2.06	2.25	1.622	2.02	2.27	1.57
Spring	Untreated	No. 1	2.08	2.00	1.90			
		No. 5*	/	/	/			
		No. 9	1.99	2.02	1.95	2.04	2.01	1.93
	1:20	No. 4R*	/	/	/			

		/	/	/			
	No. 12R	0.98	0.49	1.10	0.98	0.49	1.10
1:100	No. 3	2.14	2.17	2.11			
	No. 7	2.15	2.13	2.18	2.10	2.11	2.09
	No. 11	2.00	2.03	1.97			
1:200 (and 250)	No. 2R	1.87	2.11	1.50			
	No. 6R	1.92	2.16	1.54	2.01	2.19	1.73
	No. 10	2.23	2.30	2.15			
Average					1.77	1.78	1.63

Note: "/" indicates that the data is unavailable due to incomplete droplet size distribution from measurement
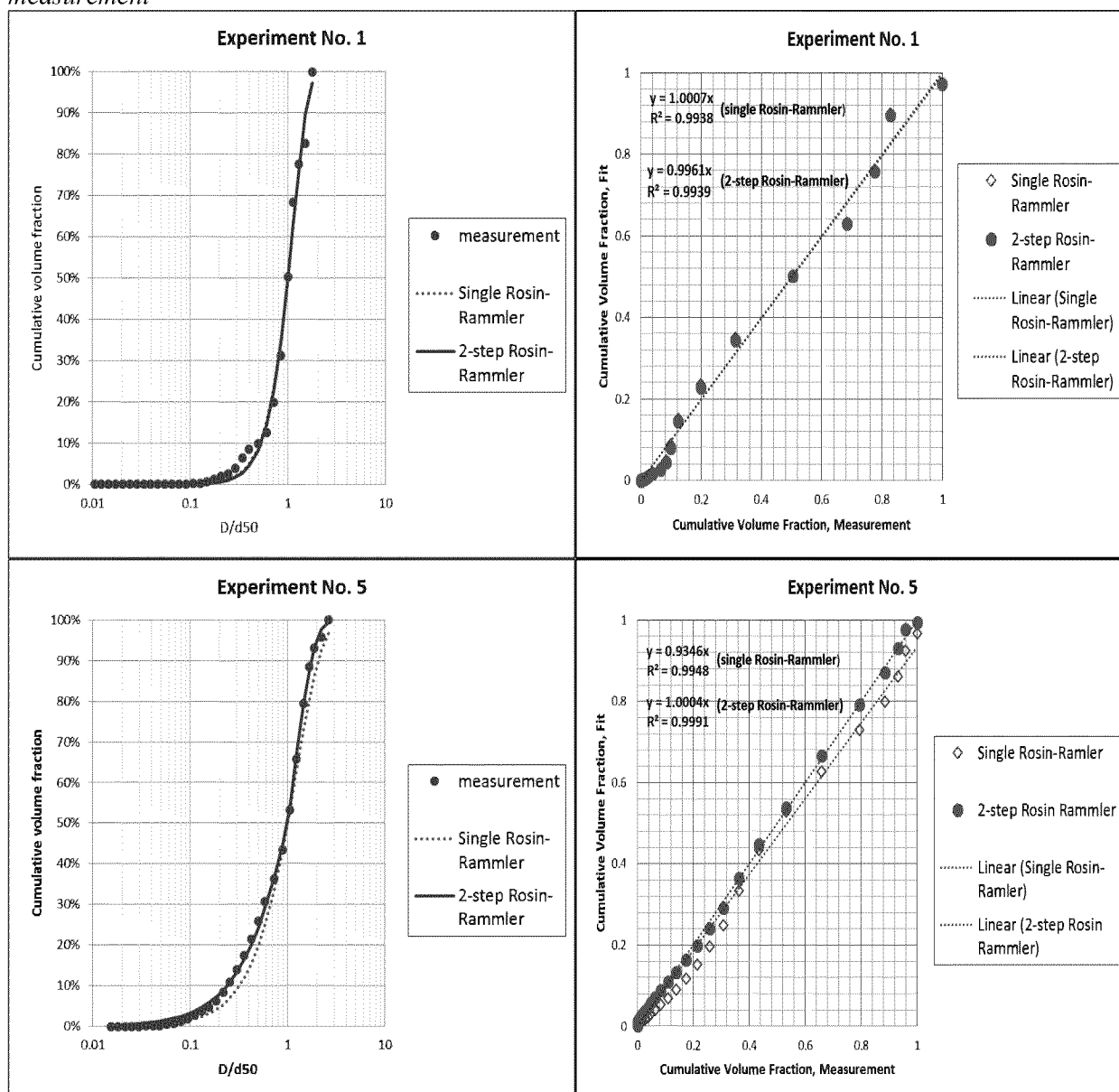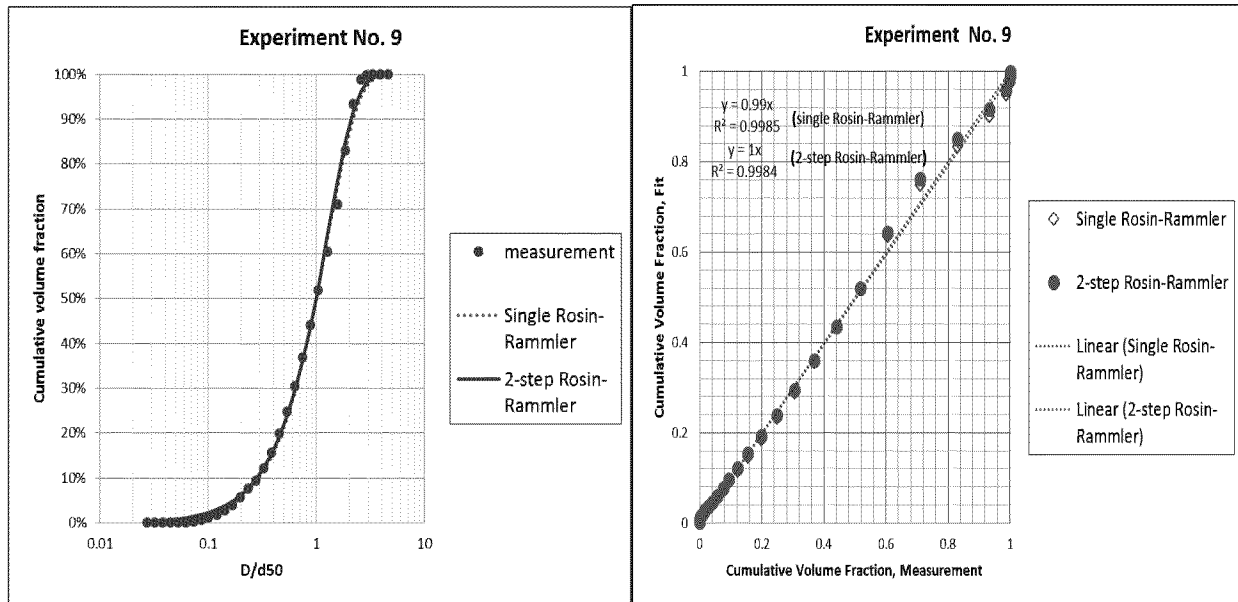
Figure 27: Cumulative distribution of d/d_{50} and regression results for IFO-120 with DOR = 0 in spring conditions

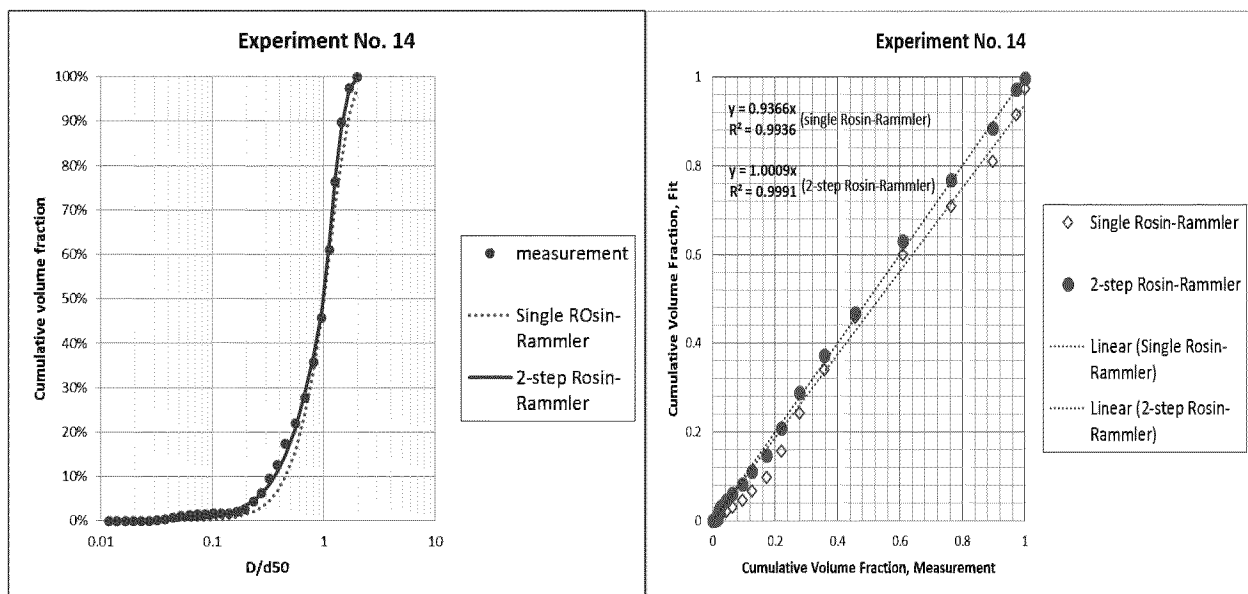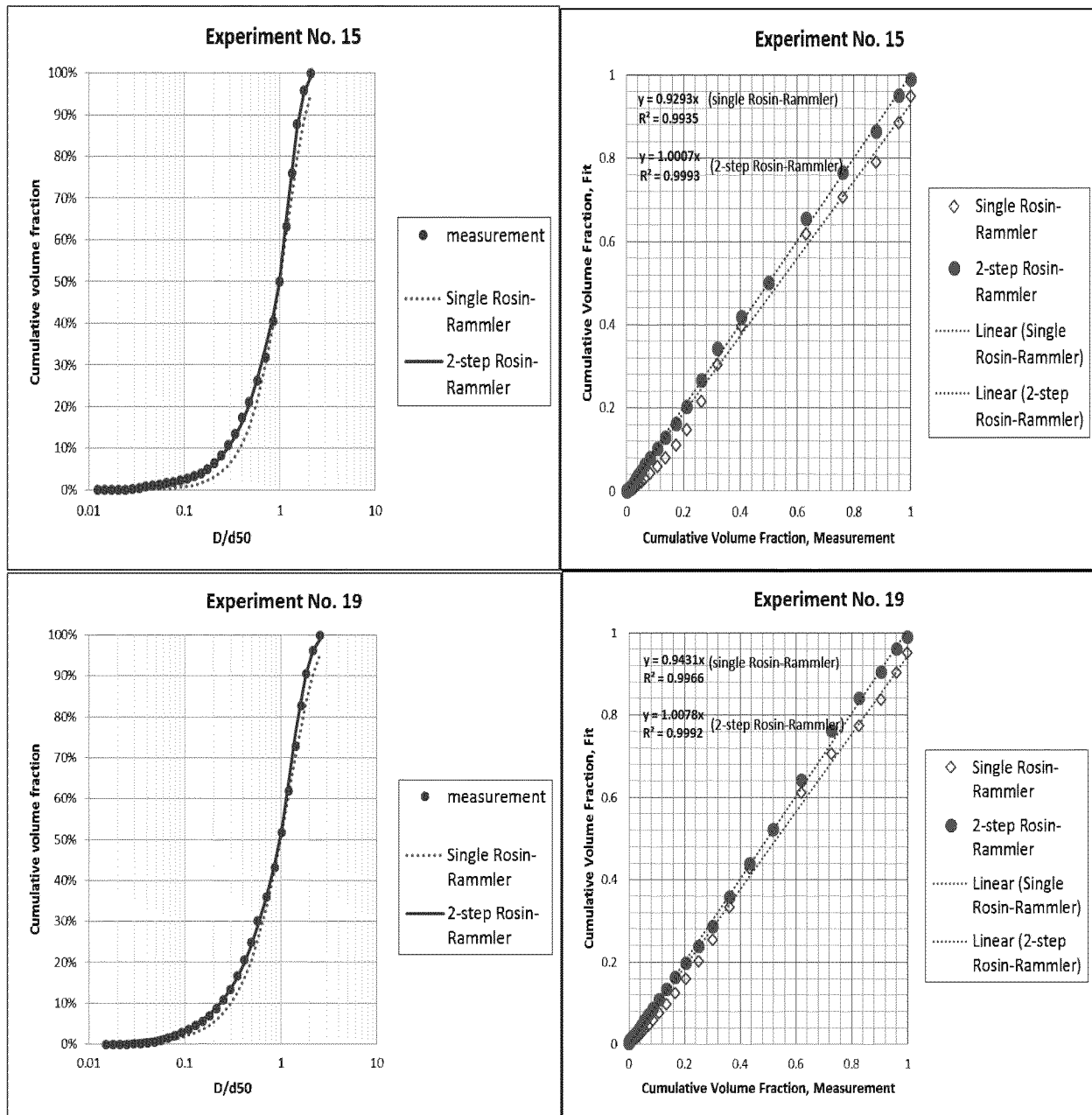*(Note: the left figures are distributions and the right ones are regression results)*
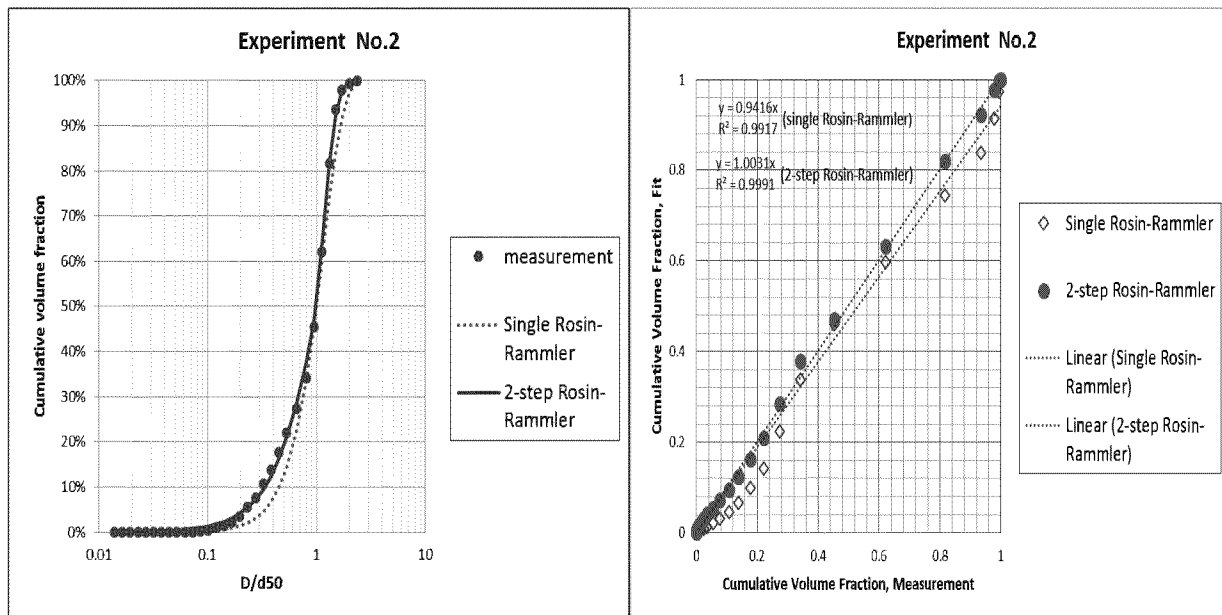
Figure 28: Cumulative distribution of d/d_{50} and regression results for IFO-120 with DOR = 1:250 in spring conditions

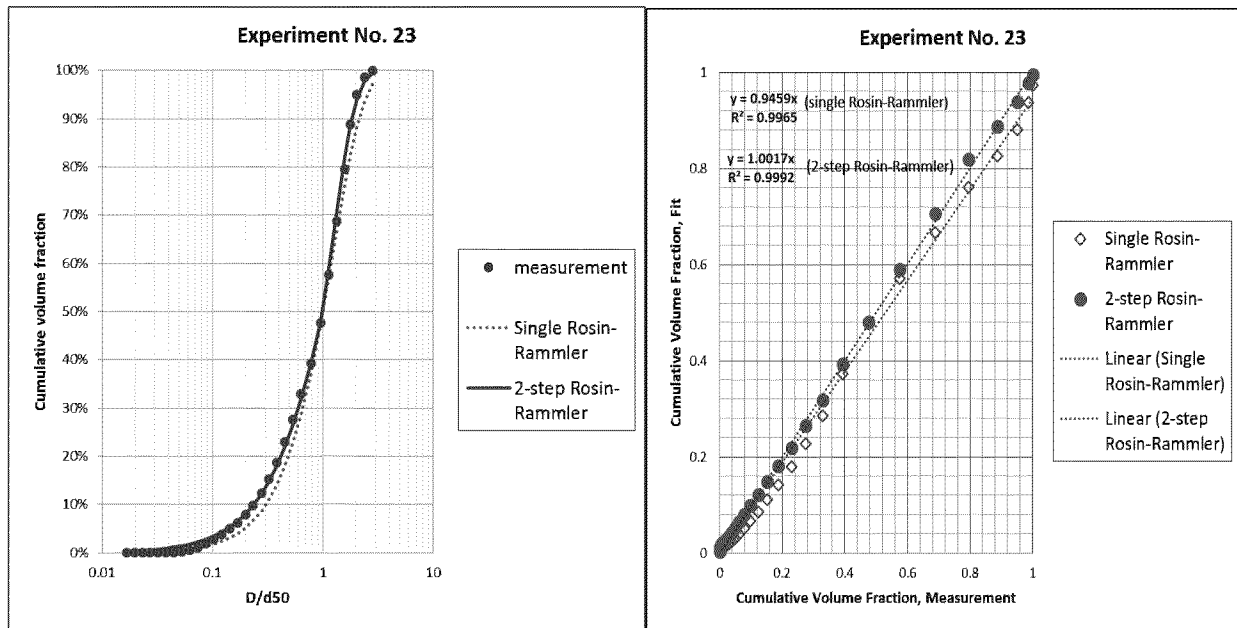*(Note: the left figures are distributions and the right ones are regression results)*
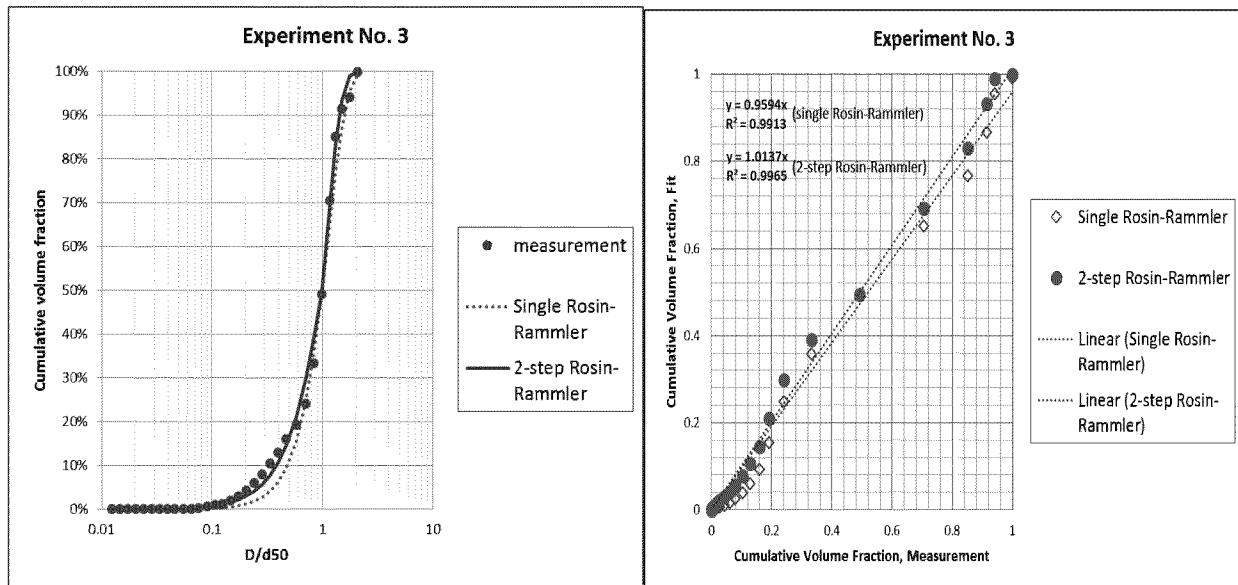
Figure 29: Cumulative distribution of d/d_{50} and regression results for IFO-120 with DOR = 1:100 in spring conditions

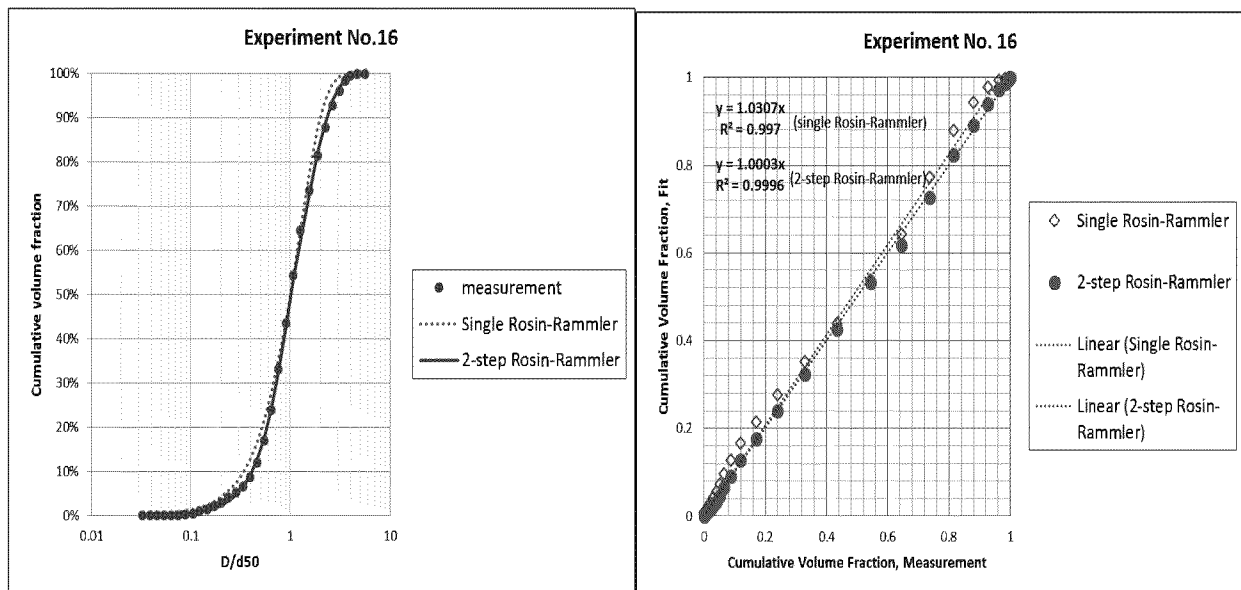*(Note: the left figures are distributions and the right ones are regression results)*
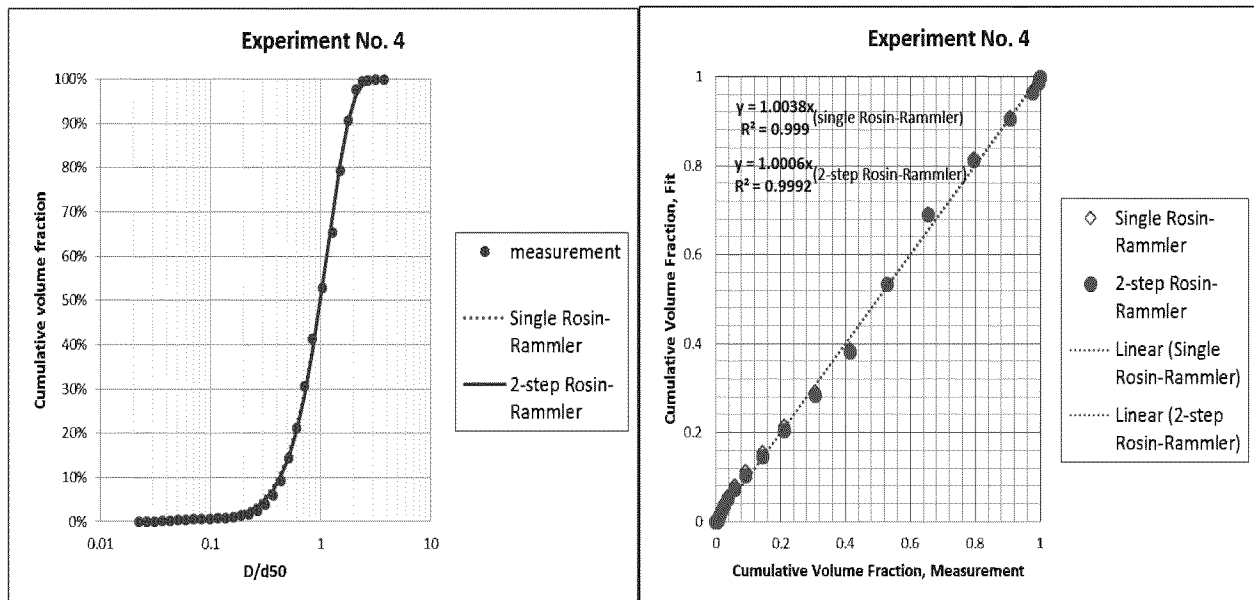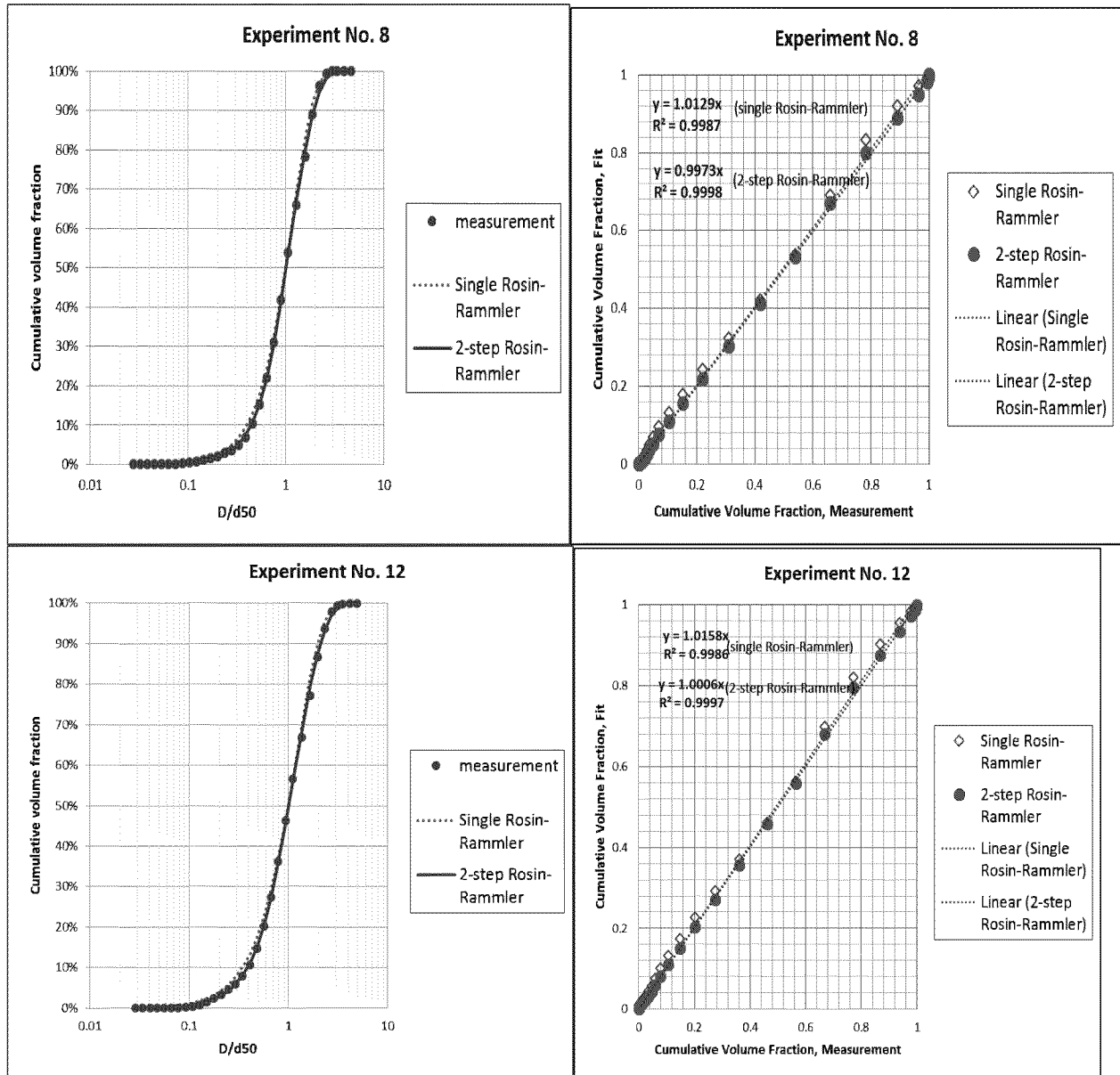
Figure 30: Cumulative distribution of d/d$_{50}$ and regression results for IFO-120 with DOR = 1:25 in spring conditions

(Note: the left figures are distributions and the right ones are regression results)
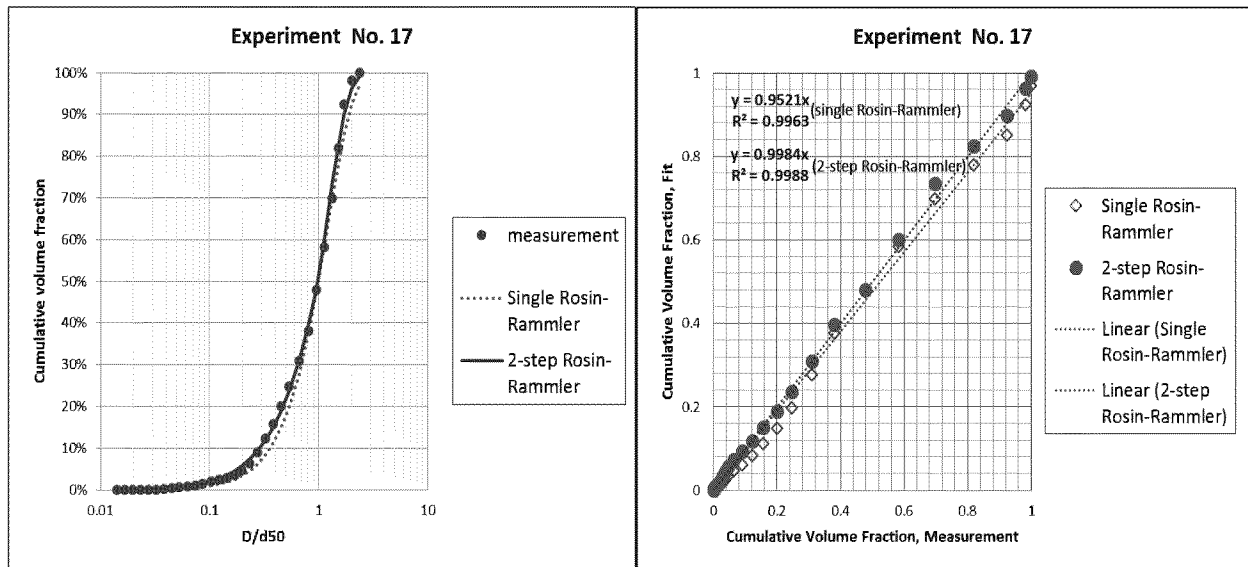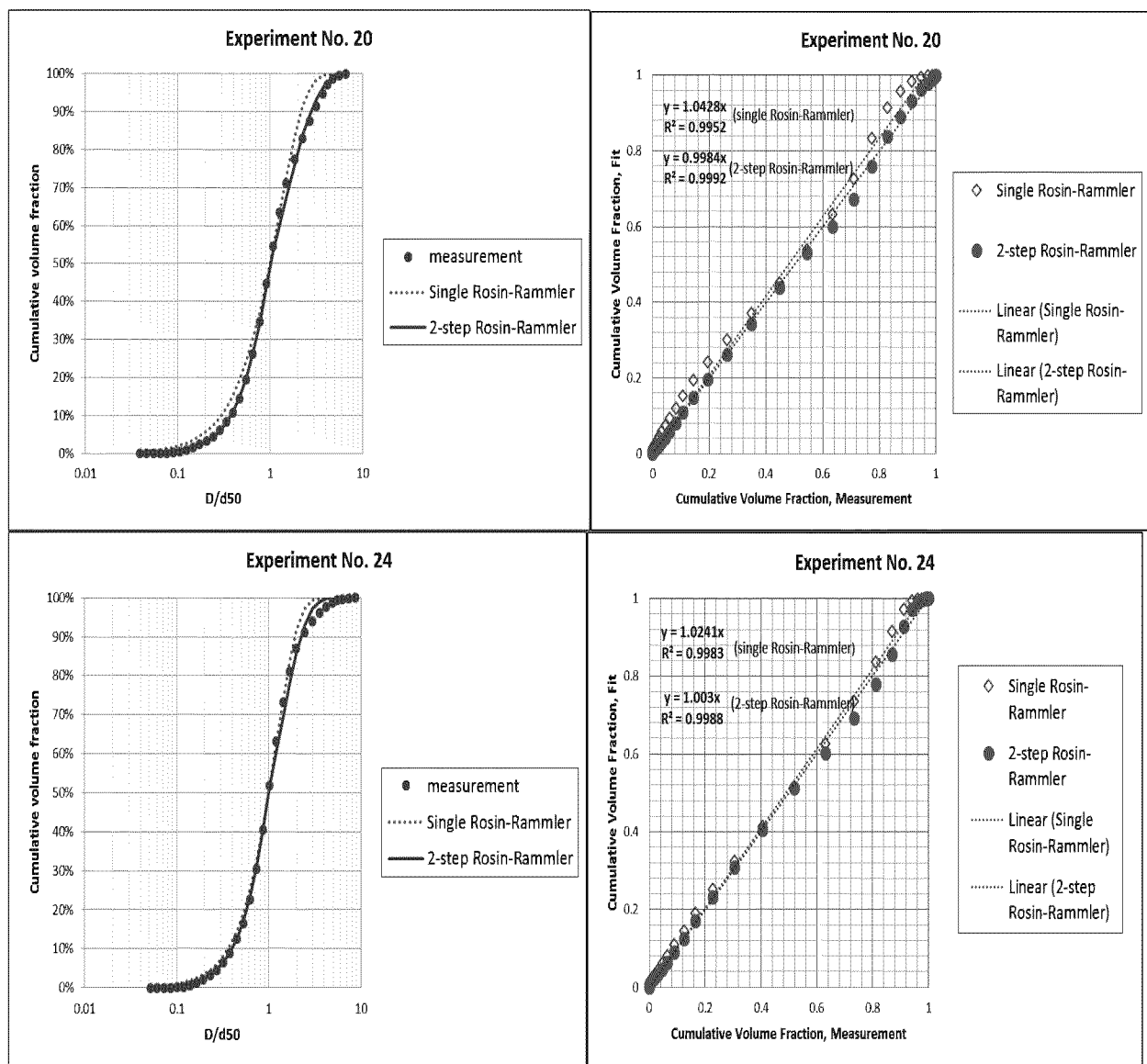
Figure 31: Cumulative distribution of d/d_{50} and regression results for IFO-120 with DOR = 0 in summer conditions

(Note: the left figures are distributions and the right ones are regression results)

Figure 32: Cumulative distribution of d/d_{50} and regression results for IFO-120 with DOR = 1.200 in summer conditions

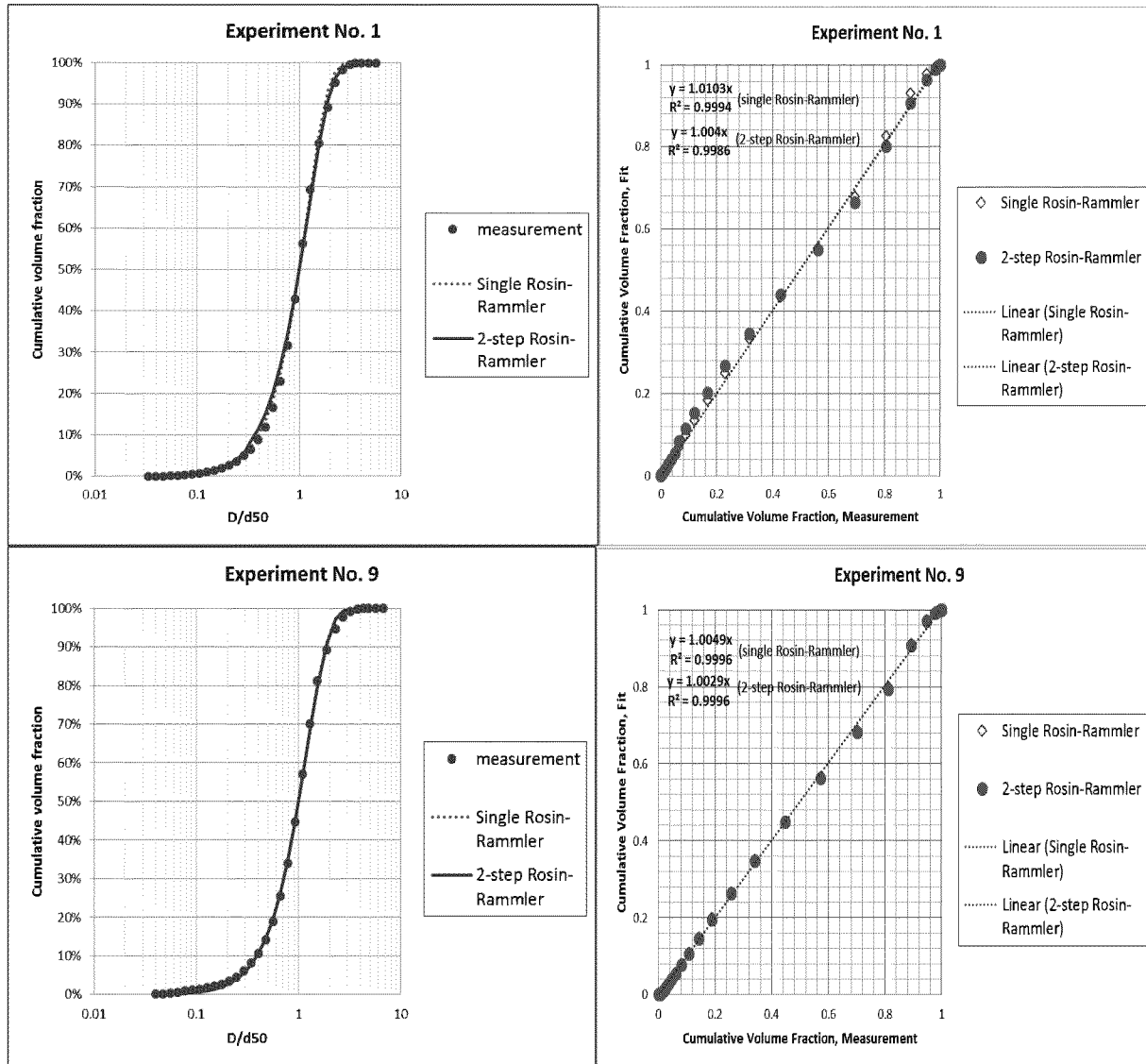*(Note: the left figures are distributions and the right ones are regression results)*

Experiment No. 15

Experiment No. 19

Figure 33: Cumulative distribution of d/d_{50} and regression results for IFO-120 with DOR =1: 100 in summer conditions

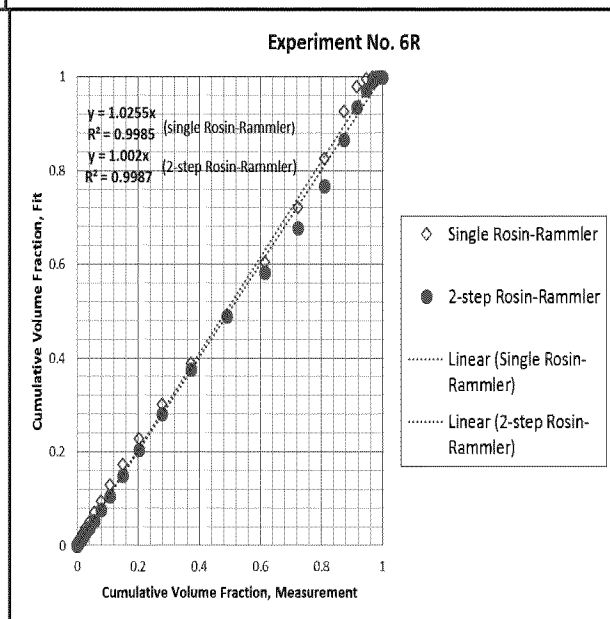*(Note: the left figures are distributions and the right ones are regression results)*
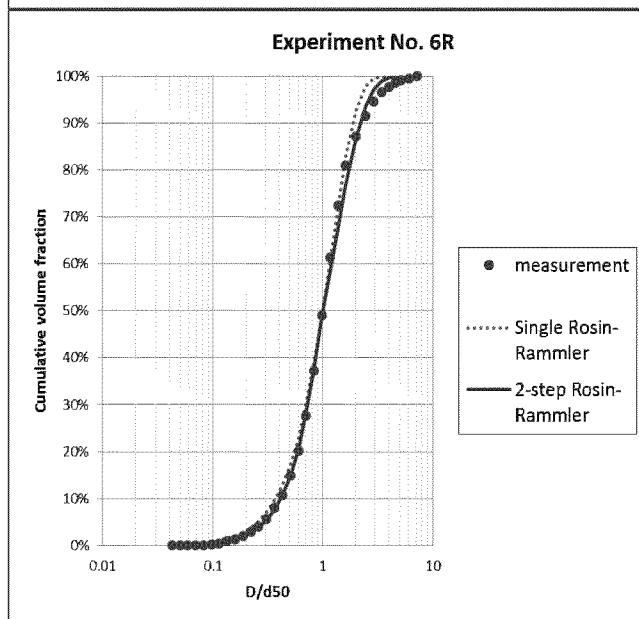
Figure 34: Cumulative distribution of d/d$_{50}$ and regression results for IFO-120 with DOR = 1:20 in summer conditions

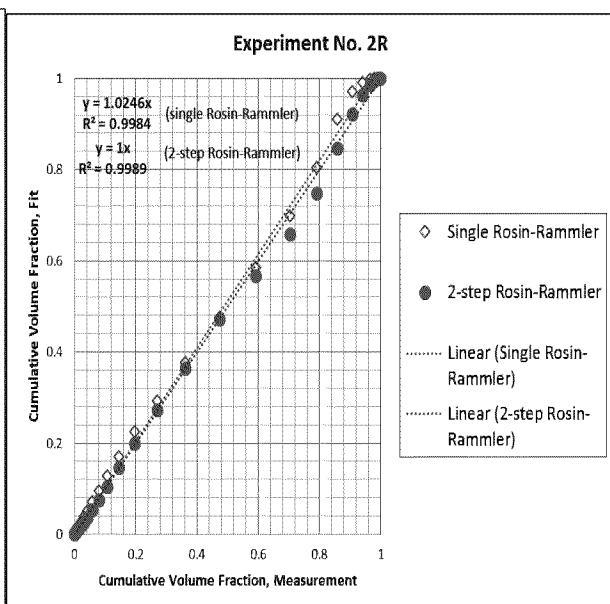*(Note: the left figures are distributions and the right ones are regression results)*
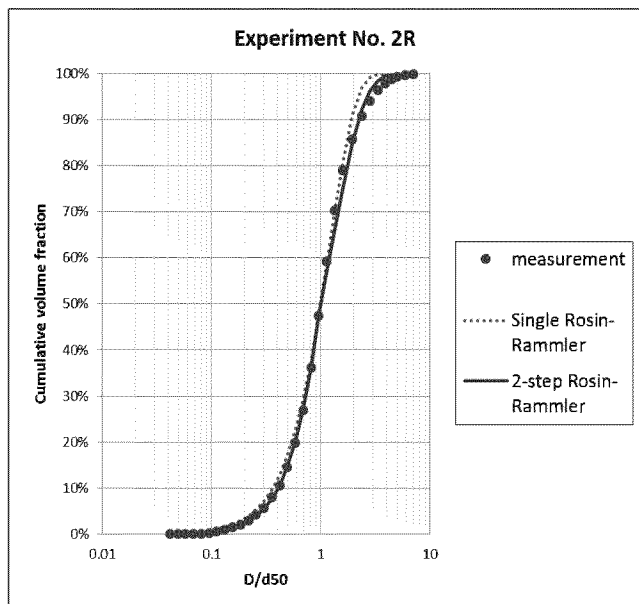
Figure 35: Cumulative distribution of d/d$_{50}$ and regression results for ANS with DOR = 0 in spring conditions

(Note: the left figures are distributions and the right ones are regression results)

Experiment No. 2R

Experiment No. 2R
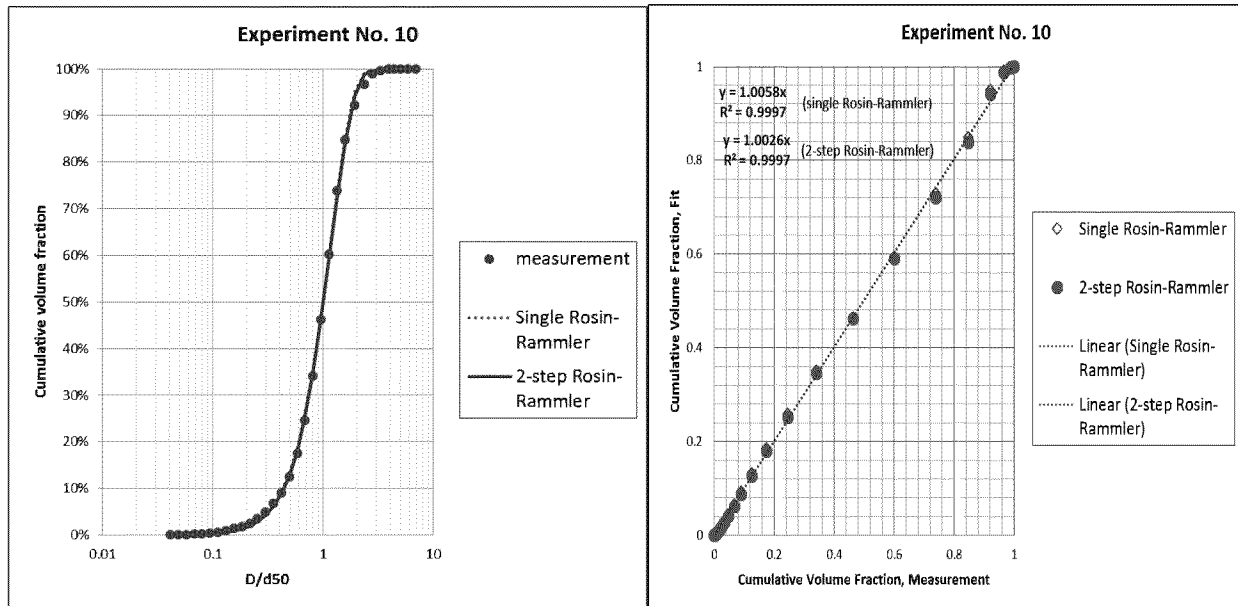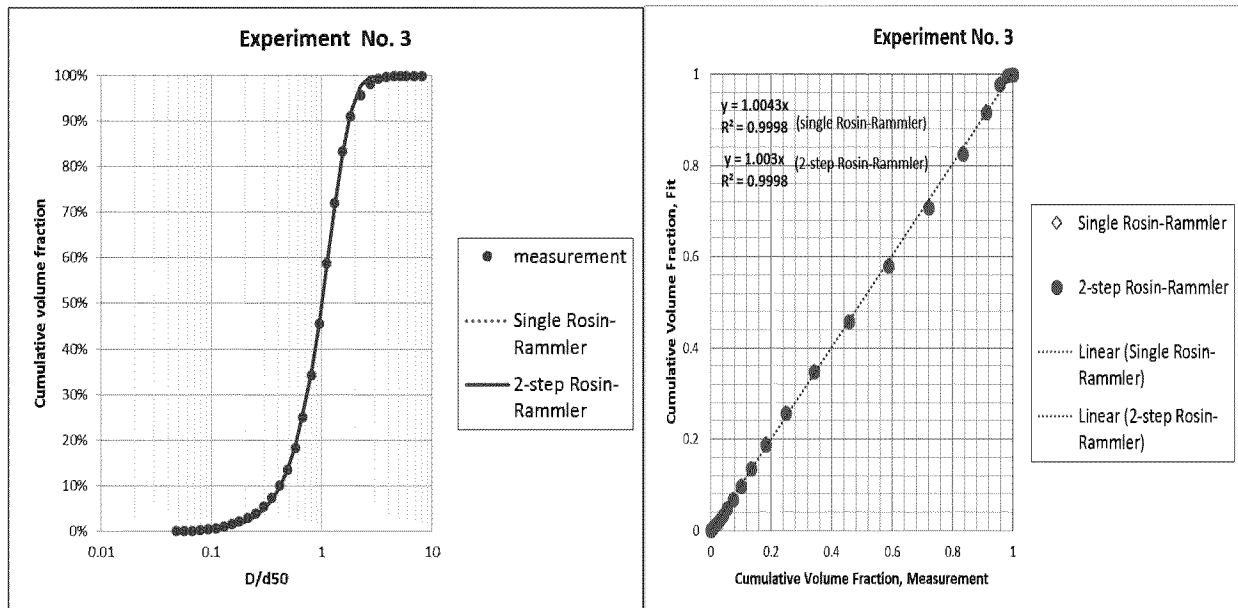
Experiment No. 6R

Experiment No. 6R

Figure 36: Cumulative distribution of d/d_{50} and regression results for ANS with DOR = 1:200 or (250) in spring conditions

(Note: the left figures are distributions and the right ones are regression results, Experiment No. 10 is DOR=1:250)
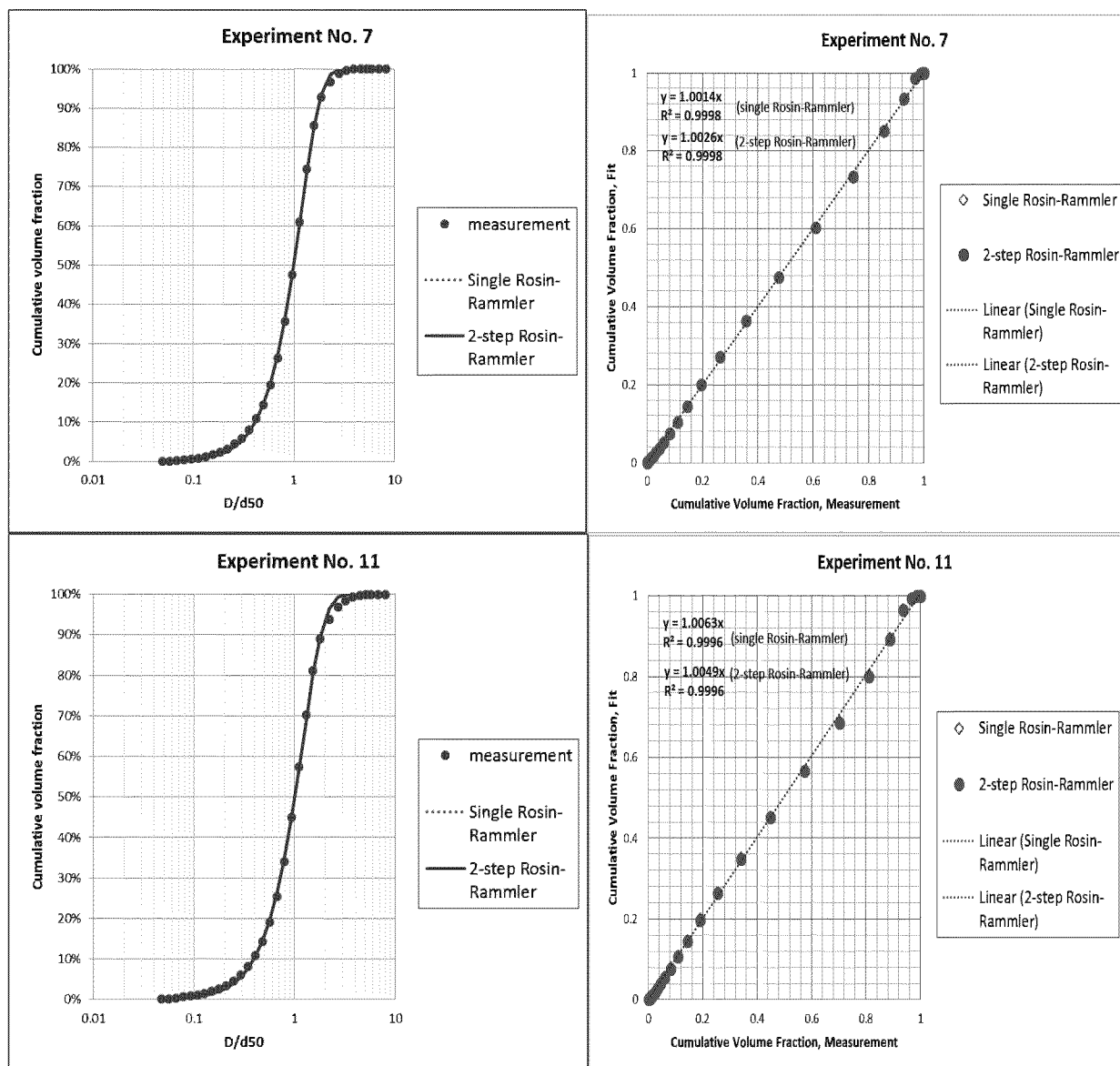
Figure 37: Cumulative distribution of d/d_{50} and regression results for ANS with DOR = 1:100 in spring conditions

(Note: the left figures are distributions and the right ones are regression results)

Figure 38: Cumulative distribution of d/d50 and regression results for ANS with DOR = 1:20 in spring conditions

(Note: the left figures are distributions and the right ones are regression results)
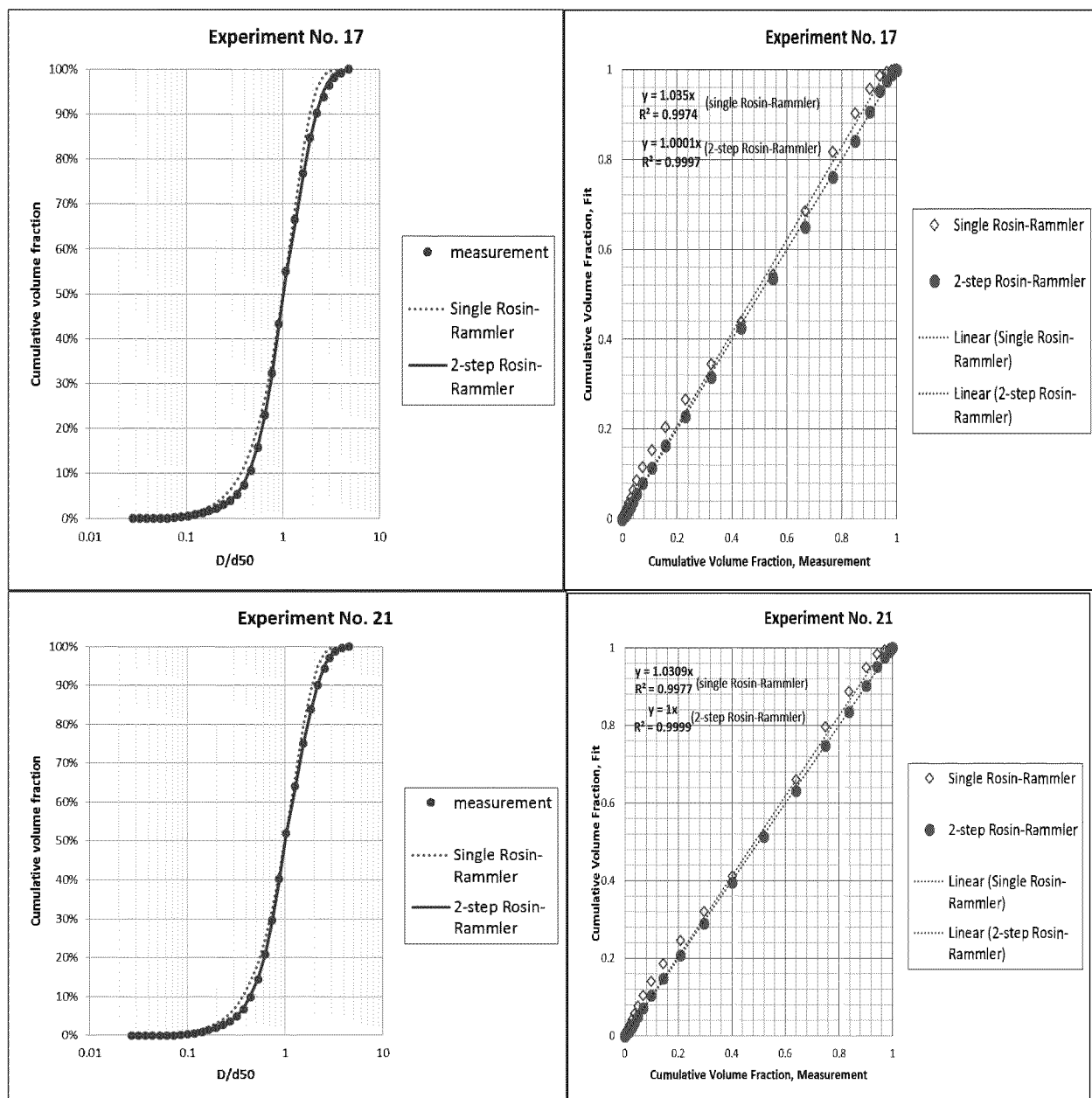
Figure 39: Cumulative distribution of d/d₅₀ and regression results for ANS with DOR = 0 in summer conditions

(Note: the left figures are distributions and the right ones are regression results)

Experiment No. 14

Experiment No. 14

Experiment No. 18

Experiment No. 18
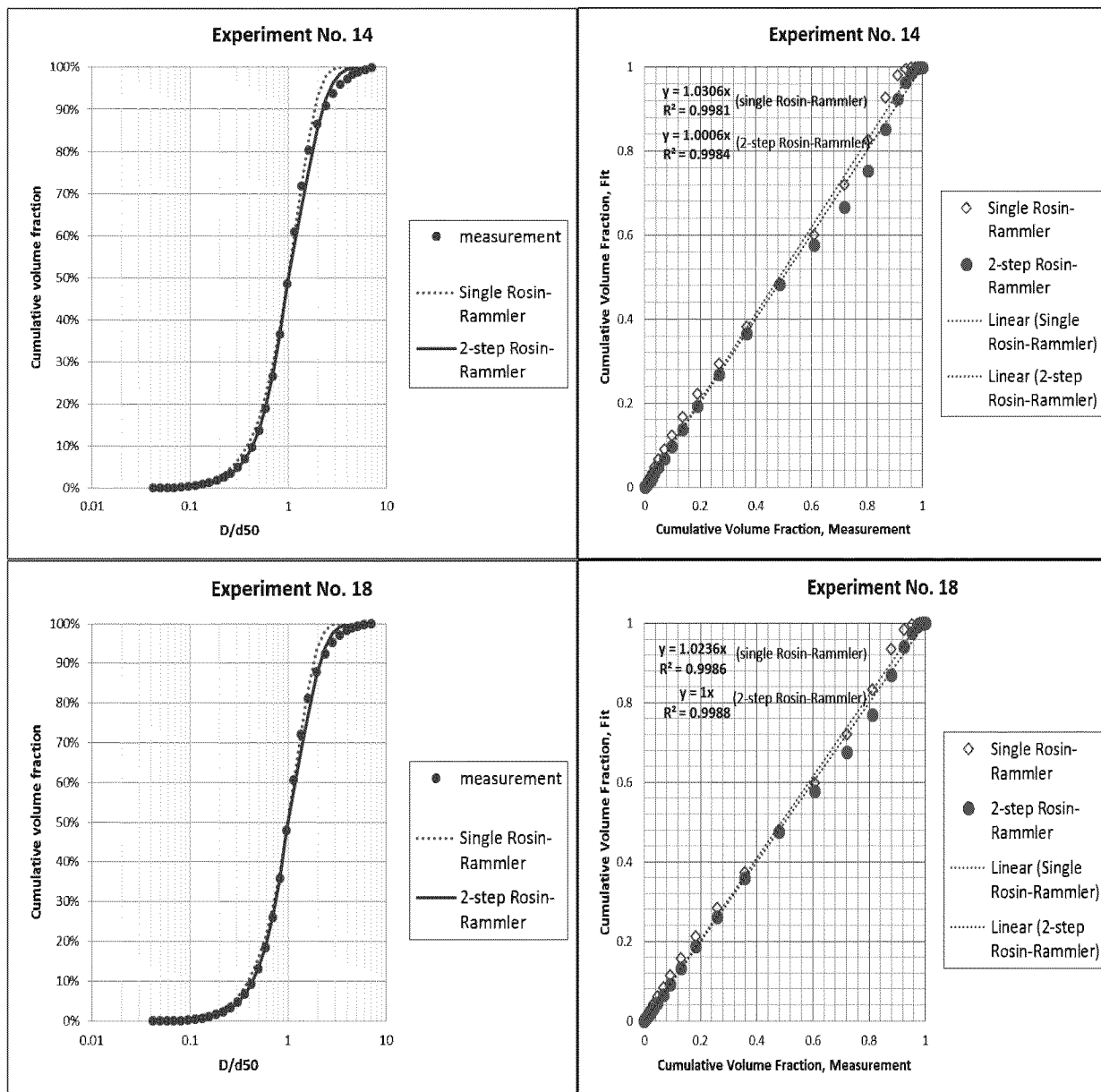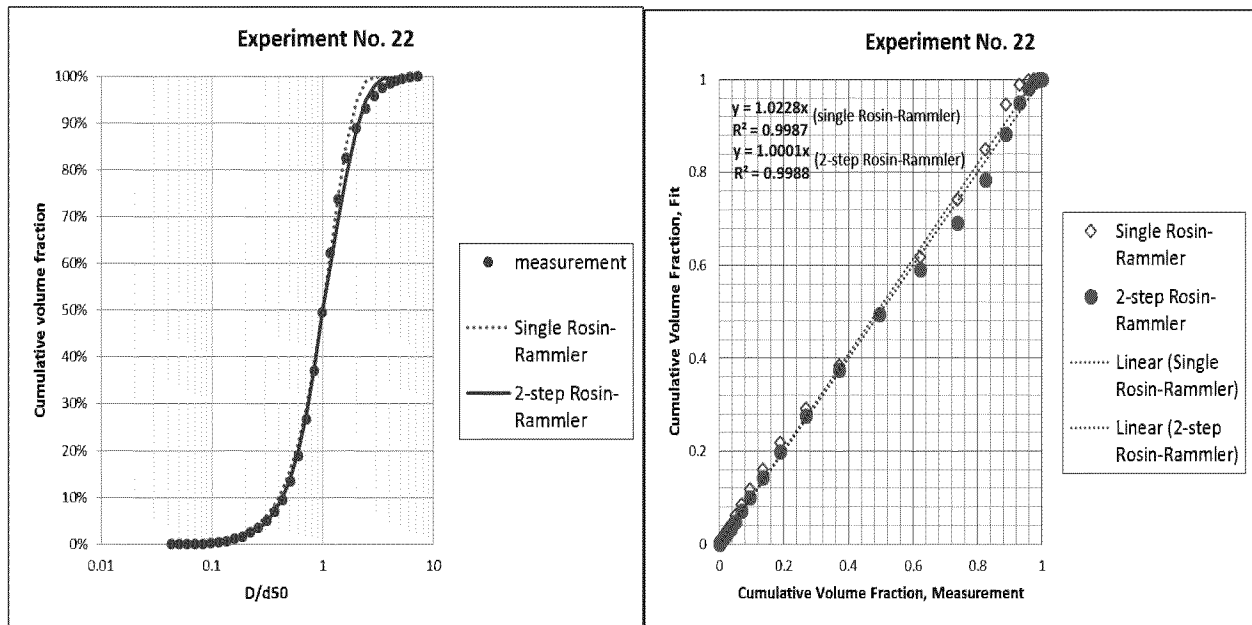
Figure 40: Cumulative distribution of d/d_{50} and regression results for ANS with DOR = 1:200 in summer conditions

(Note: the left figures are distributions and the right ones are regression results)
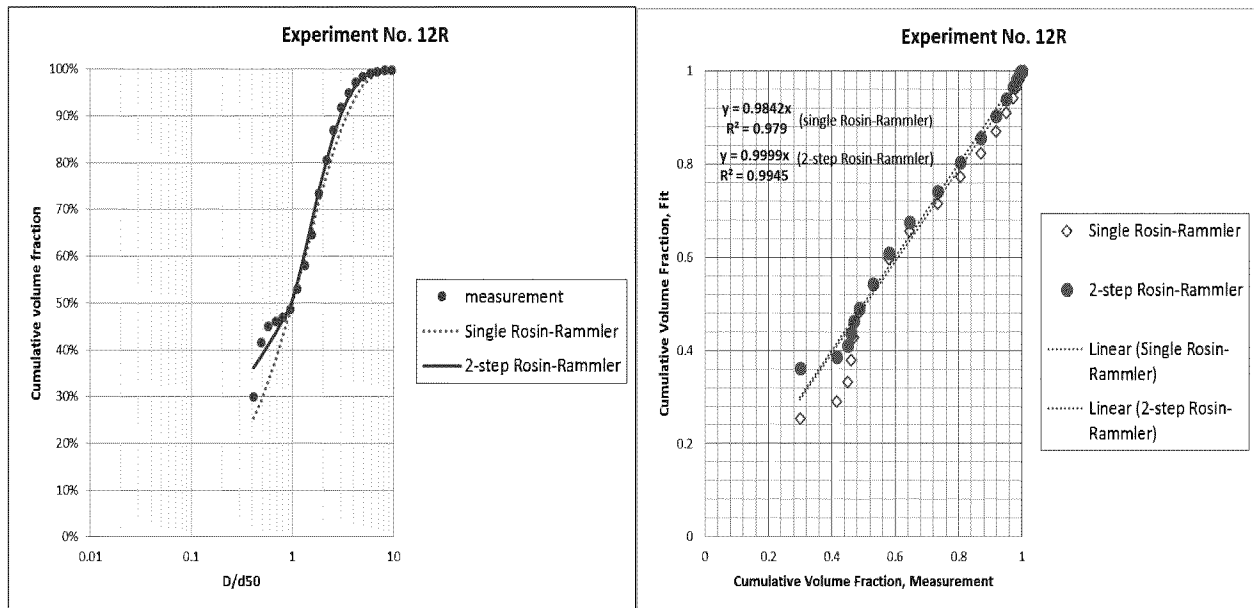
Figure 41: Cumulative distribution of d/d₅₀ and regression results for ANS with DOR =1:100 in summer conditions

(Note: the left figures are distributions and the right ones are regression results)
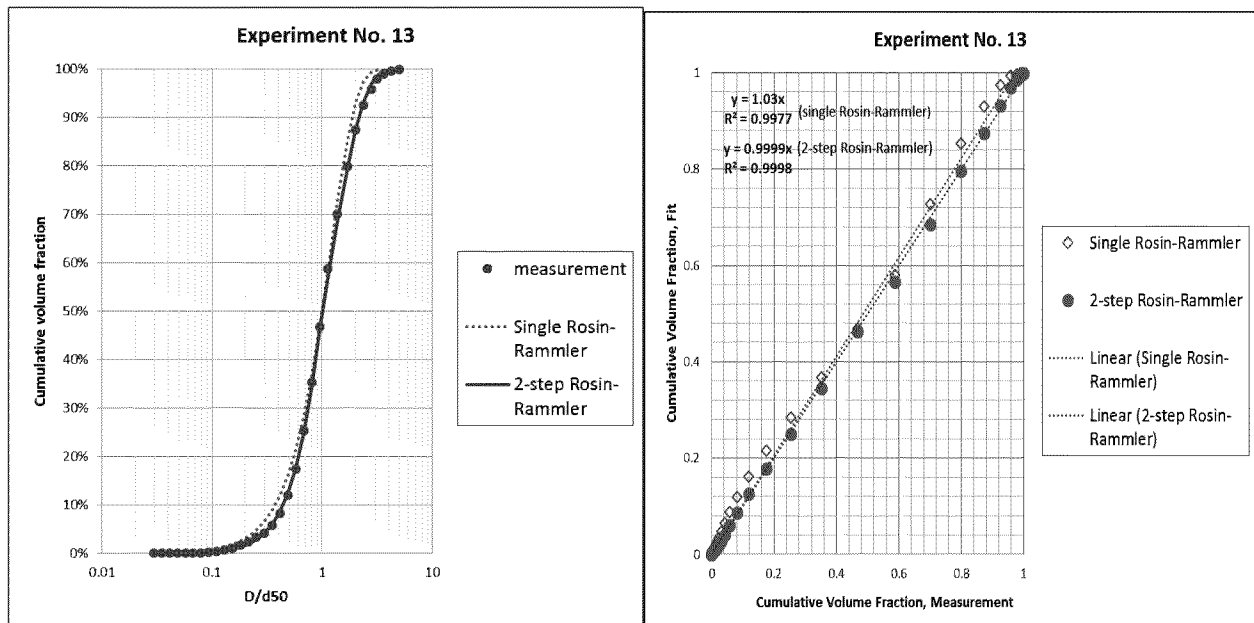
Experiment No. 16

Experiment No. 16

Experiment No. 20

Experiment No. 20

Figure 42: Cumulative distribution of d/d50 and regression results for ANS with DOR = 1:20 in summer conditions

(*Note: the left figures are distributions and the right ones are regression results*)
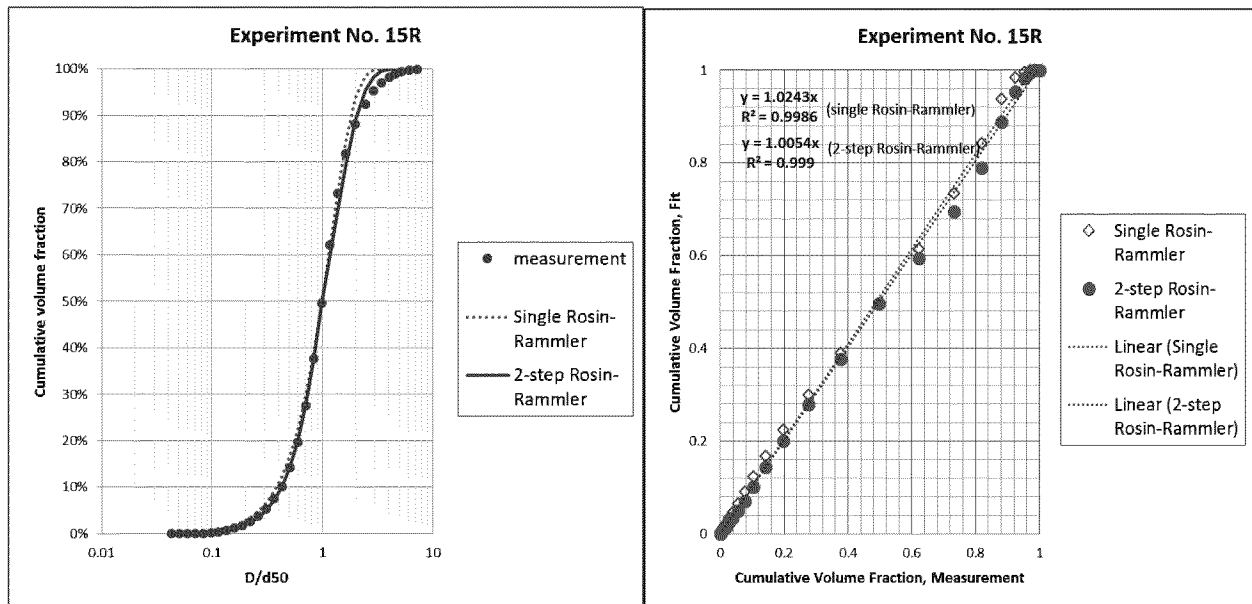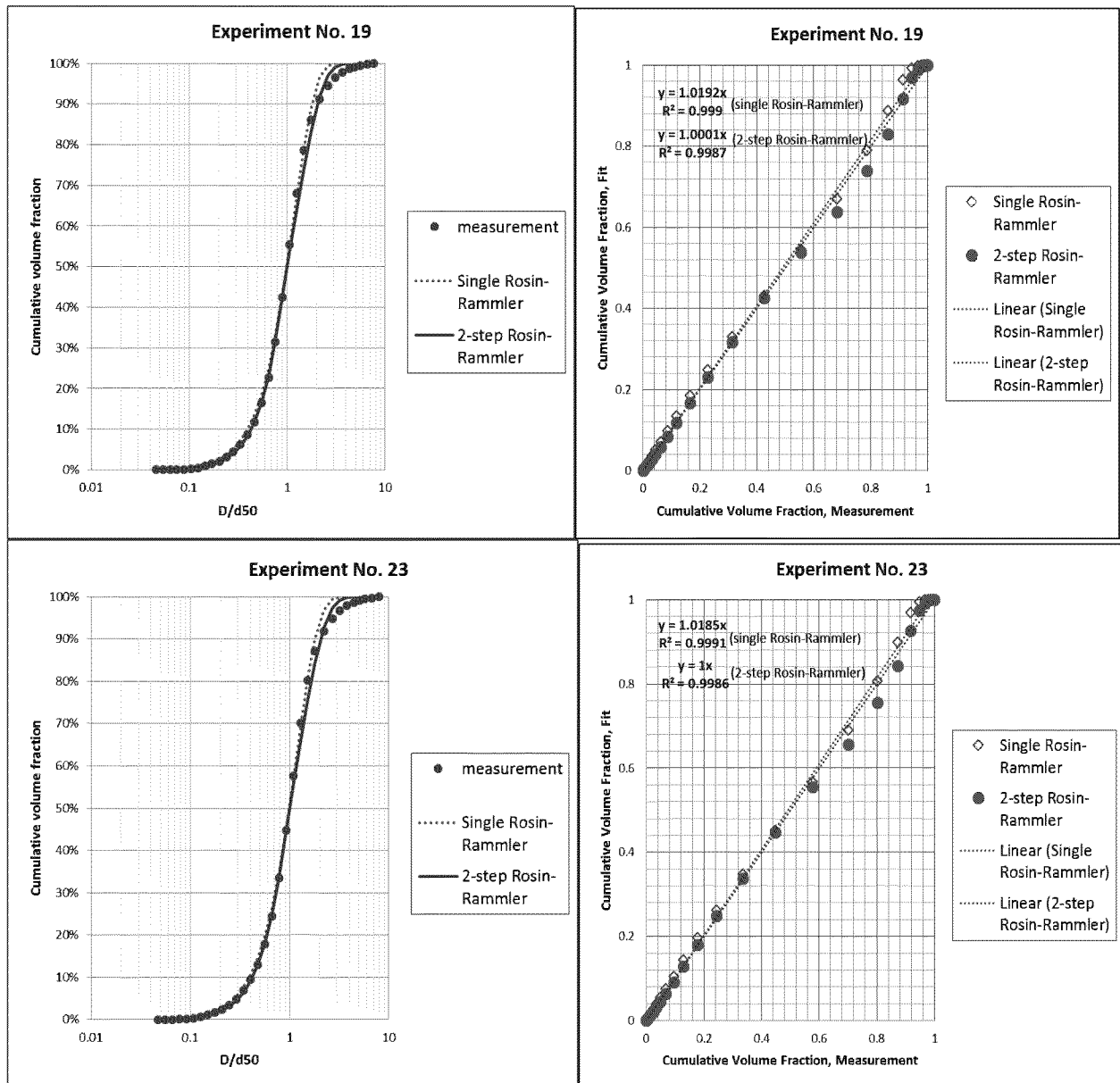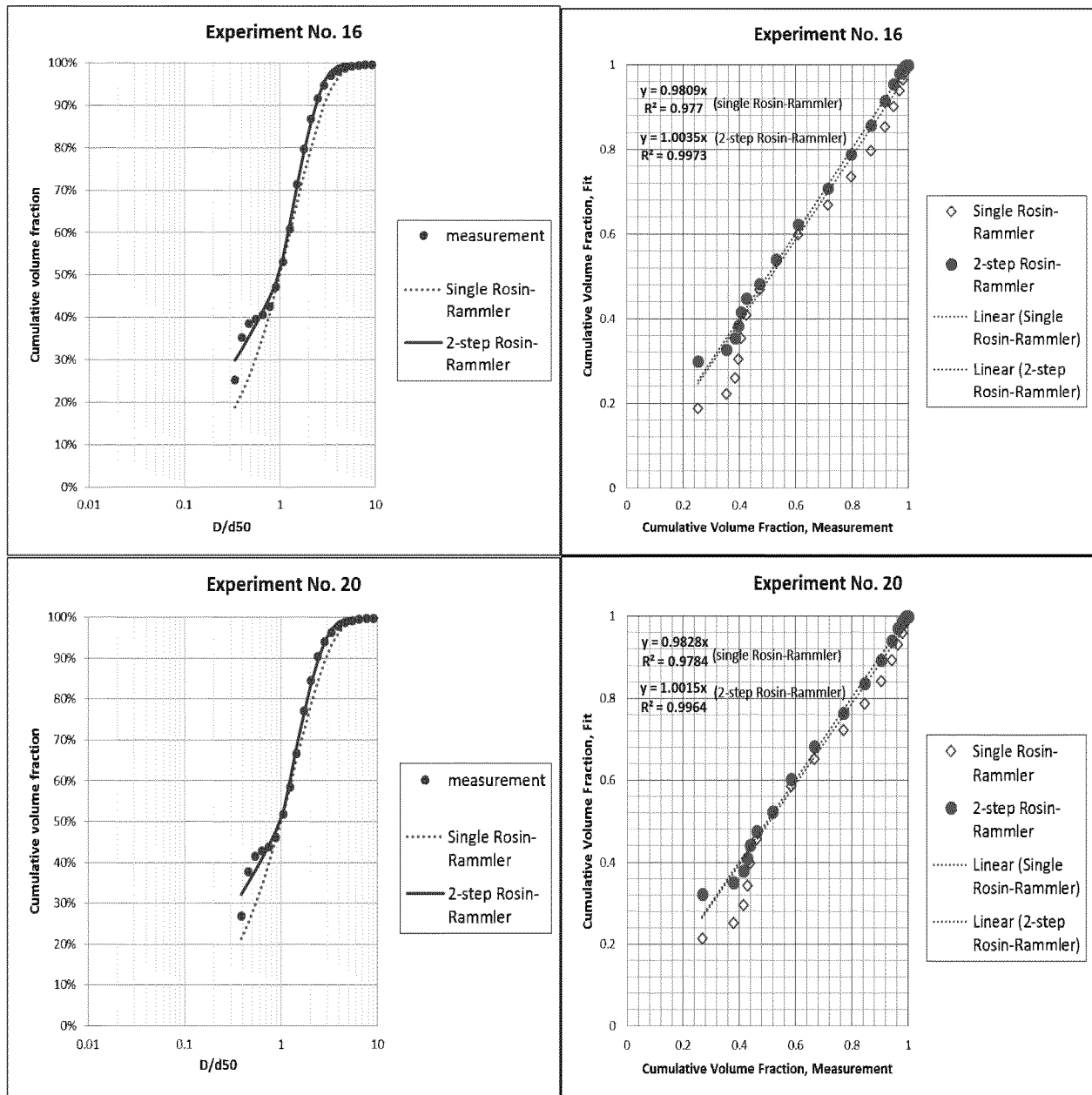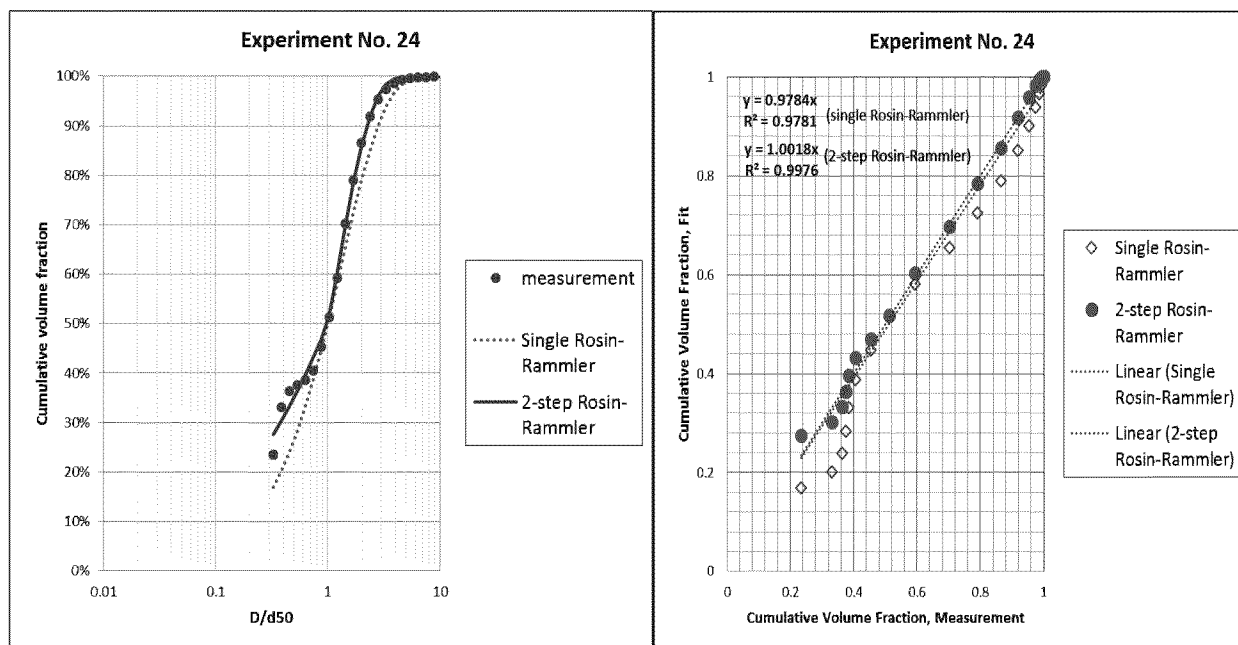

4 Summary

In this study, research has been conducted for the droplet size distributions of two types of oils (IFO-120 and ANS) release from subsurface injection with/without application of chemical dispersant in different seasonal conditions (i.e., spring and summer). Firstly, a series of experiments have been conducted via wave tank experiment by COOGER in BIO to measure the droplet sizes. These data were analyzed and utilized to determine the relative volume median diameter (d_{50}) and the peak diameter (d_p). Accordingly to the droplet size distribution and the modified Weber number approach, the Weber number (We), as well as the additional measurements on oil viscosity and IFT, the Viscosity number (Vi) and Reynold number (Re) were calculated. In addition, the relation between the droplet size distributions and dispersant-oil-ratios (DORs) has also been analyzed. Finally, the corresponding empirical coefficients have been determined for the droplet size prediction.

Furthermore, the data analysis has also indicated that the distributions of the data with $d/d_{50} <= 1$ and $d/d_{50} > 1$ are significantly varied. Thus, it would be difficult and/or inaccurate to predict the measured IFO-120 and ANS data by only a single distribution. Therefore, a two-step Rosin-Rammler approach was introduced by advancing from the Rosin-Rammler approach proved by Johansen et al. (2013). The proposed approach uses two separate spreading coefficients: α_1 for $d/d_{50} <= 1$ and α_2 for $d/d_{50} > 1$, providing better fit of the data in all cases. The regression coefficients for the two-step Rosin-Rammler are higher than which for the original single one in most of the case, indicating the advantage of the proposed two-step Rosin-Rammler approach.

In general, the chemical dispersant plays an importance role in reduce the droplet size of ANS no matter in spring or summer conditions. The effectiveness of dispersant in reducing droplet size is higher on ANS than which on IFO-120. There may be thresholds for the dose of chemical dispersant to some oils (e.g., IFO-120) but will need further experiments to analyze. There may also be over dose of dispersant to some oils (e.g., ANS) when the DOR is high, eventually affecting the droplet size distribution. Future experiment will also need for this particular issue.

The measured IFT for the IFO-120 and ANS with different DORs appeared significant difference compared with the ones measured from SINTEF for the modified Weber number approach. This may due to the characteristics of different oil. Further experiments will be needed to address this issue.

Acknowledgement

References

Buist, I.A., W. M. Pistruzak, and D.F. Dickins, "DOME Petroleum's Oil and Gas Undersea Ice Study", in Proceedings of the Fourth Arctic Marine Oilspill Program Technical Seminar, Ottawa, ON, 1:647-686, 1981,

Brandvik, P. J., et al. (2013). "Droplet breakup in subsurface oil releases - Part 1: Experimental study of droplet breakup and effectiveness of dispersant injection." Marine Pollution Bulletin 73(1): 319-326.

Chen, F. H. and P. D. Yapa (2007). "Estimating the oil droplet size distributions in deepwater oil spills." Journal of Hydraulic Engineering-Asce 133(2): 197-207.

Chen, F. H. and P. D. Yapa (2003). "A model for simulating deepwater oil and gas blowouts - Part II: Comparison of numerical simulations with "deepspill" field experiments." Journal of Hydraulic Research 41(4): 353-365.

The Federal Interagency Solutions Group, Oil Budget Calculator Science and Engineering Team (2010). Oil Budget Calculator: Deepwater Horizon: 217.

Johansen, O., et al. (2003). "DeepSpill - Field study of a simulated oil and gas blowout in deep water." Spill Science & Technology Bulletin 8(5-6): 433-443.

Johansen, O., et al. (2013). "Droplet breakup in subsea oil releases - Part 2: Predictions of droplet size distributions with and without injection of chemical dispersants." Marine Pollution Bulletin 73(1): 327-335.

Louis J. Thibodeaux, et al. (2011). "Marine Oil Fate: Knowledge Gaps, Basic Research, and Development Needs; A Perspective Based on the Deepwater Horizon Spill." Environmental

Engineering Science 28(2): 87-93.

Lefebvre, A. H. (1989). Atomization and Sprays, Taylor & Francis, P. 421

Stephen M. Masutani and E. E. Adams (2001). Experimental Study of Multi-Phase Plumes with Application to Deep Ocean Oil Spills. Deep Spill JIP, University of Hawaii (UH) and Massachusetts Institute of Technology (MIT). 147.

Topham, D.R., Hydrodynamics of an Oilwell Blowout, Beaufort Sea Technical Report #33, Department of the Environment, Victoria, BC, 52p., 1975

Wang, C. Y. and R. V. Calabrese (1986). "Drop Breakup in Turbulent Stirred-Tank Contactors .2. Relative Influence of Viscosity and Interfacial Tension." Aiche Journal 32(4): 667-676.

Zhao, L., et al. (2014). "Evolution of droplets in subsea oil and gas blowouts: Development and validation of the numerical model VDROP-J." Marine Pollution Bulletin 83(1): 58-69.

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Mike Fulton - NOAA Federal
Sent: Mon 2/9/2015 3:15:01 PM
Subject: Re: following up

Hi Robyn,

I hope you're well. Would you have time for a quick call sometime this week? I've got a couple of dispersant (finasol, corexit) questions.

Mike

On Tue, Sep 23, 2014 at 11:18 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

> Thanks Robyn. I think we are about to receive the oil we requested from BP. Fingers crossed.
>
> Mike
>
> On Fri, Sep 19, 2014 at 10:13 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:
>
>> Hi Mike,
>>
>> I heard from EPA OEM that the oil purchase is approved but that it hasn't been ordered. That is the only information I have received. I did speak with Debbie Payton on Wednesday and she mentioned that her office has gotten some oil that may be available to you. I hope that is the case. There is some irony that we are all trying to conduct oil research that is critical for regulation, yet cannot access the oil. Sigh.
>>
>> Cheers,
>>
>> Robyn
>>
>> <>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>
>>
>> Robyn N. Conmy, Ph.D.
>>
>> Research Ecologist
>>
>> USEPA/NRMRL/LRPCD
>>
>> 26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

--
Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief
Center for Coastal Environmental Health and
Biomolecular Research (CCEHBR)
USDOC/NOAA/NOS/NCCOS
219 Fort Johnson Road
Charleston, SC 29412-9110
voice: (843) 762-8576 fax: (843) 762-8700
e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

--
Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief
Center for Coastal Environmental Health and
Biomolecular Research (CCEHBR)
USDOC/NOAA/NOS/NCCOS
219 Fort Johnson Road
Charleston, SC 29412-9110
voice: (843) 762-8576 fax: (843) 762-8700
e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Kremer, Fran
Sent: Tue 3/1/2016 9:14:48 PM
Subject: RE: oil docs
Technical Review Form_363_1A_wave tank report Kremer review.pdf
E12PG00037_Draft Final Report_OEM_sept2015_fk.docx

Hi Robyn,

Here's the review form and the document with track changes – I added comments in with
OEM's.

Fran

Fran Kremer, Ph.D.

Senior Science Advisor

Office of Research and Development/NRMRL and

Office of Enforcement and Compliance Assurance

U.S. Environmental Protection Agency

26 W. M. L. King Dr.

Cincinnati, OH 45268

513-569-7346

From: Conmy, Robyn
Sent: Thursday, February 18, 2016 10:02 AM
To: Kremer, Fran <Kremer.Fran@epa.gov>
Subject: RE: oil docs

Ideally, the first week of March would be best. Attached are the comments from OEM on the
text. Take a look and let me know if you're up to the task. Like I mentioned earlier, I do think
the document has received rigorous review through an unconventional approach. Now it's just a
matter of obtaining the signed official technical review form from OLEM and ORD.

Thanks,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Kremer, Fran
Sent: Thursday, February 18, 2016 9:36 AM
To: Conmy, Robyn <Conmy.Robyn@epa.gov>
Subject: oil docs

Hi Robyn,

The docs are still there. When do you want the review done?

Fran

Fran Kremer, Ph.D.

Senior Science Advisor

Office of Research and Development/NRMRL and

Office of Enforcement and Compliance Assurance

U.S. Environmental Protection Agency

26 W. M. L. King Dr.

Cincinnati, OH 45268

513-569-7346

To: Conmy, Robyn[Conmy.Robyn@epa.gov]; fingasmerv@shaw.ca[fingasmerv@shaw.ca]; tchazen@utk.edu[tchazen@utk.edu]; robert.jones@noaa.gov[robert.jones@noaa.gov]; mandyjoye@gmail.com[mandyjoye@gmail.com]; mbleigh@alaska.edu[mbleigh@alaska.edu]; karl.linden@colorado.edu[karl.linden@colorado.edu]; kmmcfarlin@alaska.edu[kmmcfarlin@alaska.edu]; msmiles@lsu.edu[msmiles@lsu.edu]; thomas.s.coolbaugh@exxonmobil.com[thomas.s.coolbaugh@exxonmobil.com]; mathijs.smit@shell.com[mathijs.smit@shell.com]; Sprenger, Mark[Sprenger.Mark@epa.gov]
Cc: nancy.kinner@unh.edu[nancy.kinner@unh.edu]; 'Ian Gaudreau'[iangaudreau@gmail.com]; Mandsager, Kathy[kathy.mandsager@unh.edu]
From: Mandsager, Kathy
Sent: Mon 9/28/2015 9:30:45 PM
Subject: Degradation Group appendix review
20145.09.28_Appendix for Degradation Group to review.xlsx

Degradation Group,

As follow-up to our call on Friday, a list of publications for your review are located here>>https://unh.box.com/s/wwn2juyzfkgt5bd20n4s8e8bo3uq5t93.

To make it easier for your review, we have a spreadsheet (attached) for your input. Please simple say "yes" or "no" in each of the 2 columns next to each publication. Share any comments in order to clarify or support your vote on each publication.

Please submit by **Friday 30 October.**

Kathy Mandsager

Program Coordinator

Coastal Response Research Center

Center for Spills and Environmental Hazards

234 Gregg Hall, Colovos Rd

University of New Hampshire

Durham, NH 03824

603.862.1545

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Holder, Edith
Sent: Thur 6/11/2015 5:48:34 PM
Subject: RE: SEA BRAT #4 Sample Inquiry

Robyn,

Re DE tests

I have BF filled with seawater and at temperature and prepared labels.

I just obtained the bung to open the oil drum from Josh.

I plan to open the drum and sample the oil tomorrow and run the first tests.

I'm on my way down to collect your signature.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Conmy, Robyn
Sent: Thursday, June 11, 2015 1:07 PM
To: Holder, Edith
Subject: RE: SEA BRAT #4 Sample Inquiry

Elisha can respond.

BTW – how are the DE tests going?

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Holder, Edith
Sent: Thursday, June 11, 2015 12:44 PM
To: Conmy, Robyn
Cc: Bryan, Elisha
Subject: FW: SEA BRAT #4 Sample Inquiry

Robyn,

Is this OK for Elisha to respond to the manufacturer or do you or someone in OEM want to take this as the protocol is in the final stages of approval?

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Bryan, Elisha
Sent: Thursday, June 11, 2015 11:51 AM
To: Holder, Edith
Subject: Fw: SEA BRAT #4 Sample Inquiry

Edie,

Its been so long, I had to think what MDL of DCM was, lol.

I found a good contact for Sea Brat Dispersant, but he wants data sent to him. I assume it is the same as SWA, can not send anything, but will be published for everyone to see and none of the Dispersants will be directly named in the publication?

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: John Sheffield <alabastercorp@gmail.com>
Sent: Thursday, June 11, 2015 11:31 AM
To: Bryan, Elisha
Subject: Re: SEA BRAT #4 Sample Inquiry

Hello,

I can provide a sample if you pay shipping.

But I want written/ email of all the test results, publications, etc.

Where are the result going to be published, etc.

John Sheffield

On Thu, Jun 11, 2015 at 10:19 AM, Bryan, Elisha <Bryan.Elisha@epa.gov> wrote:

Good Afternoon,

The U.S. Environmental Protection Agency will be conducting a series of Dispersant Efficacy experiments using the newly proposed Baffled Flask Test for inclusion in the 40 CFR Appendix C to Part 300 Subpart J. I am a contractor with EPA's Office of Research and Development, National Risk Management Research

Laboratory (NRMRL), Land Remediation and Pollution Control Division (LRPCD), working on this research.

As your product is listed on the U.S. EPA National Contingency Plan Product Schedule, we would like to include your product in our research and are interested in procuring a small quantity. I am contacting all manufacturers listed so that we can take into consideration the different characteristics of the dispersants.

This research will not change the current status of your product on the Product Schedule. More information on the proposed revisions and who to contact for comments can be found here: https://www.federalregister.gov/articles/2015/01/22/2015-00544/national-oil-and-hazardous-substances-pollution-contingency-plan#h-44.

Could you please send me a price quote for one liter / quart of *SEA BRAT #4*?

Thank you,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Robyn Conmy
Sent: Mon 2/2/2015 2:02:27 PM
Subject: Fwd: PWSRCAC
dispersants_salinity_and_pws.pdf

---------- Forwarded message ----------
From: **Robyn Conmy** <conmy.robyn@gmail.com>
Date: Sat, Jan 31, 2015 at 2:28 PM
Subject: Re: PWSRCAC
To: Robyn Conmy <conmy.robyn@gmail.com>

On Sat, Jan 31, 2015 at 1:58 PM, Robyn Conmy <conmy.robyn@gmail.com> wrote:

http://www.pwsrcac.org/wp-
content/uploads/filebase/programs/environmental_monitoring/dispersants/dispersants_salinity_and_pws.pdf

Dispersants, Salinity and Prince William Sound

for

Prince William Sound Regional Citizens' Advisory Council (PWSRCAC)
Anchorage, Alaska

by

Merv Fingas
Environmental Technology Centre
Environment Canada

December, 2004

Abstract

This paper is a summary of the effects of water salinity on chemical dispersion, especially those effects related to effectiveness. Surfactants are the active ingredient in dispersants. The surfactant is more lipophilic, or oil-loving, in freshwater and increases in hydrophilicity (or water-loving) as the salinity rises. The stability of the resulting droplets is also dependent on salinity. This is due to the increasing ionic strength of the water as salinity rises. As the salinity rises above a certain point, which depends on the particular type of surfactant, this increased force results in more surfactant molecules leaving the oil drop entirely. While the theoretical possibility of freshwater dispersants exist, the stability of dispersions in less saline waters would be less.

This report reviews several older dispersant tests. Data from these tests were separated from more recent data because older testing procedures and analytical methods are not as accurate as today's methods. Newer testing is reviewed as well. This testing is marked by the use of analysis by chromatography and very strict protocols in operating the dispersant tests themselves. These tests are marked by having standard deviations less that 10% and often less than 5%. The conclusions from both recent and older studies are the same.

The general surfactant literature was reviewed for the effects of salinity on surfactants and surfactant phenomena. There is a body of literature on the use of surfactants for secondary oil recovery. There are some commonalities among the many findings. Recovery efficiency falls off at both high and low salinities. The salinity at which surfactant efficiency peaks is very dependent on the structure of the specific surfactant. Several studies on the interaction of specific hydrocarbons and surfactants were reviewed. The consensus of these papers is that the solubility of the hydrocarbon increases with increasing salinity and is low at low salinities. The interfacial tension of water and oil changes with surfactant and salinity. The interfacial tension is higher at lower salinities. The optimal interfacial tension is generally achieved at salinities of between 25 to 35 o/oo. A number of physical systems involving surfactants and salinity changes are reported in the literature. Included in these is the finding that the stability of microemulsions is greater at salinities of 25 to 35o/oo. Some workers found that the stability of systems was very low in fresh water or in water with salinities of < 10 o/oo.

Some field studies of dispersant application were conducted in the freshwater environment. While effectiveness was not specifically measured, it was noted in both series of studies that effectiveness may have been low. In the one study, the investigators noted that the surfactants had poor effectiveness and stability in freshwater. In this particular case, the dispersion lasted only for about an hour and the dispersion was limited to a few centimetres. In another case, it was noted that there was oil around the edges of the dispersed pond within a short time of dispersant application.

Some effects studies were conducted under varying salinity conditions. In one study, naphthalene and a,b napthol sulphate uptake were studied under different salinity conditions. There were no significant differences at different salinities, although, naphthalene uptake was somewhat higher under low salinity conditions. Another study examined the induction of hsp60 protein in golden-brown algae. It was found that greater salinity reduced the effects of the simulated oil spills on the algae.

The varying salinities of the waters in Prince William Sound were described and summarized. There are areas around the Sound of low salinity. Dispersant applications in these areas would result in reduced dispersant effectiveness.

The following are the overall conclusions of this study.

a) The effectiveness of conventional and currently available dispersants is very low at 0 o/oo or sometimes they are even completely ineffective. This is consistent with physical studies described in the surfactant literature.

b) Dispersant effectiveness peaks at 20 to 40 o/oo. This may depend on the type of dispersant. Corexit 9500 appears to be less sensitive to salinity but still shows a peak at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and with others at about 35 o/oo.

c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and as it exceeds this value.

d) While there is some evidence for a temperature-salinity interaction, as noted in the data of Moles et al., 2002, there are not enough data to make solid conclusions.

e) Recent data are largely taken using Corexit 9527 and Corexit 9500. Since these have the same surfactant packages, there is a concern that the results may be more relevant to these formulations than to others.

f) Observations on two field trials in freshwater appear to indicate that the laboratory tests are correct in concluding very low freshwater effectiveness.

g) There were few studies on the biological effects of oil with varying salinity. There are not sufficient data to reach conclusions.

h) The findings in the dispersant literature summarized in this study are in agreement with the theoretical and basic surfactant literature.

i) The salinity of the waters in Prince William Sound is typically high in the centre of the Sound, but is sometimes low, especially near river outfalls, and in fjords with tidewater glaciers. The salinities in these areas, often less than 15 o/oo, will result in lower dispersant effectiveness.

Summary and Issues

Overall
　　The relationship between salinity and overall effectiveness of dispersants is reviewed in this document.

Specific Issues
The following is a summary of the specific issues and technical concerns related to salinity and dispersants.
　　1. It is very clear that salinity changes the effectiveness of conventional oil spill dispersants. In water with low salinity, these products have low effectiveness, even approaching zero.
　　2. There is very clear agreement on the effect of salinity and the relative changes this causes in dispersant effectiveness. There are a few exceptions, but these are all in the older literature and relate to studies with questionable analytical methods.
　　3. There are several outstanding questions: whether or not salinity changes any toxicity thresholds and whether there is an interaction between temperature and salinity.

Conclusions
The following are the overall conclusions of this study.
　　a) In waters with a salinity of 0 o/oo, conventional and currently available dispersant have a very low effectiveness or are sometimes even completely ineffective. This is consistent with physical studies in the surfactant literature.
　　b) Dispersant effectiveness peaks in waters with a salinity ranging from 20 to 40 o/oo. This may depend on the type of dispersant. Corexit 9500 appears to be less sensitive to salinity but still peaks at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and at about 35 o/oo with others.
　　c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and after it exceeds this value. The curves for this salinity effect appear to be Gaussian.
　　d) While there is some evidence for a temperature-salinity interaction as noted in the data of Moles et al., 2002, there is not enough data to make solid conclusions.
　　e) Recent data are almost exclusively measured using Corexit 9527 and Corexit 9500. Since these have the same surfactant packages, there is a concern that the results may be more relevant to these formulations than to all possible formulations.
　　f) Observations on two field trials in freshwater appear to indicate that the laboratory tests are correct in concluding very low dispersant effectiveness in freshwater.
　　g) There were few studies on the biological effects of varying salinity and given oil exposure. There are not sufficient data to reach conclusions.
　　h) The findings in the dispersant literature reviewed here are in agreement with those in the theoretical and basic surfactant literature. The effect of ionic strength and salinity on both hydrophilic-lipophilic balance and stability is the reason for the decreased effectiveness noted at low salinities and the same decrease at high salinities above a certain peak of about 20 to 40 o/oo.
　　i) The waters in Prince William Sound are sometimes low in salinity, often less than 15 o/oo, especially near river outfalls and in bays. This will result in lower dispersant effectiveness.

v

List of Acronyms

ANS - Alaska North Slope - Usually referring to the crude oil mixture at the end of the pipeline

ASMB - Alberta Sweet Mixed Blend - a type of crude oil

CTAC - Cetyltrimetyl ammonium bromide (a surfactant)

CTAB - Cetyltrimetyl ammonium chloride (a surfactant)

Corexit 9527 - Brand name of a dispersant from Exxon

Corexit 9500 - Brand name of a dispersant from Exxon

DLVO - Derjaguin Landau Verway Overbeek - A reference to a theory on surfactant stabilization, with each letter referring to the author of the original theory.

DO - Dispersed oil

EPA - US Environmental Protection Agency

EXDET - An Exxon laboratory test for dispersants

GC - Gas Chromatograph, a chemical analytical technique

HLB - Hydrophilic-lipophilic balance

IFP - The French Petroleum Institute - Usually used here as a description of their laboratory test

IFT - Interfacial tension

PAH - Polynuclear Aromatic Hydrocarbons

PWSRCAC - Prince William Sound Regional Citizens' Advisory Council

RSD - Relative standard deviation

WAF - Water-Accommodated Fraction - The sum total of oil in a water sample including physically dispersed and soluble oil

Acknowledgements

Table of Contents

List of Tables

List of Figures

1.   Introduct ion

1.1   Objective

The objective of this paper is to address the issue of the effectiveness of dispersants in waters of various salinities, such as are found in Prince William Sound.

1.2   Scope

This paper covers the literature from the inception of the oil spill concern to August of 2004 and focuses primarily on issues related to variations in dispersant effectiveness caused by salinity.

1.3   Organization

The paper begins with a summary and outline of the issues. The overall effects of salinity on dispersant effectiveness are reviewed in Section 2. Laboratory testing or colorimetric measures used in older studies are reviewed in Section 3, while more recent laboratory testing is discussed in Section 4. Section 5 reviews the surfactant literature for studies on the effects of salinity. Field studies and effects studies are discussed in Section 6. The varying salinities found in the waters of Prince William Sound are discussed in Section 7. Section 8 consists of the summary and Section 9, the conclusions of this report.

The tables and figures referred to in the text have been placed at the end of the text, before Section 10, which lists the References.

2.   Review of Salinity and Dispersant Effectiveness

Dispersant effectiveness is defined as the amount of oil that the dispersant puts into the water column versus that which remains on the surface. Effectiveness as used in this report will be constant throughout.

Surfactants have varying solubilities in water and varying actions toward oil and water. The parameter used to characterize surfactants is the hydrophilic-lipophilic balance (HLB) (Becher, 1977). HLB is determined using theoretical equations that relate the length of the water-soluble portion of the surfactant to the oil-soluble portion of the surfactant. A surfactant with an HLB between 1 and 8 promotes the formation of water-in-oil emulsions and one with an HLB between 12 and 20 promotes the formation of oil-in-water emulsions. A surfactant with an HLB between 8 and 12 may promote either type of emulsion, but generally promotes oil-in-water emulsions. Dispersants have an HLB in this range.

Dispersants are oil spill treating agents formulated to disperse oil into water in the form of fine droplets. Typically, the HLB of dispersants ranges from 9 to 11. Ionic surfactants can be rated using an expanded scale and have HLBs ranging from 25 to 40. Ionic surfactants are strong water-in-oil emulsifiers, very soluble in water and relatively insoluble in oil, which generally work from the water onto any oil present. Such products disappear rapidly in the water column and are not effective on oil.

Because they are readily available at a reasonable price, however, many ionic surfactants are proposed for use as dispersants. These agents are better classified as surface-washing agents. Some dispersants contain ionic surfactants in small proportions, yielding a total HLB closer to 15 than 10. No studies have been done on the specific effect of this on effectiveness or mode of action. A typical dispersant formulation consists of a pair of non-ionic surfactants in proportions to yield an average HLB of 10 and some proportion of ionic surfactants. Studies have been done on this mixture, one of which used statistical procedures in an attempt to determine the best mixture of the three ingredients.

It is well known in surface science that the hydrophilic portion of a surfactant is strongly affected by the salinity (Becher, 1977). This is a result of ionic strength. The greater the salinity, the greater the ionic strength and thus the greater the stability of the surfactant-stabilized droplet.

Dispersants have long been noted as being less effective in less saline waters. Martinelli and Lynch (1980) noted this as a factor to be considered. Despite this knowledge, several workers presumed that effectiveness was the same or similar in less saline water. Peabody (1982) proposed dispersant use in freshwater and noted that the concerns might be the different toxicity to aquatic species. McAuliffe (1989) developed scenarios for the use of dispersants in the nearshore environment to protect the ecosystem from surface oil damage. The assumption is that there is no reduction in effectiveness with decreasing salinity and that the effectiveness is 100%. Flaherty et al. (1989) reviewed the development of guidelines for using dispersants in fresh water and also did not note any concern about the decrease in effectiveness with decreasing salinity. This indicates that the effect of salinity was not necessarily well known among all oil spill workers, particularly those not involved in full-time research.

3. Older Laboratory Testing or Colorimetric Measures

While studies were conducted on the effectiveness of dispersants early in the history of oil spill dispersants (Martinelli and Lynch, 1980), proper quantitative methods did not appear until the mid-90s. Early methods using colorimetric analysis are in question (Fingas, 1995a). One older colorimetric method of measuring laboratory dispersant effectiveness uses a small aliquot of the dispersion test water, extracts the oil, usually with methylene chloride, and then measures the colour at a specific wavelength. This value is compared to a standard curve and effectiveness calculated. The standard curve was traditionally prepared by injecting the appropriate amount of oil directly into the methylene chloride and measuring colour density. It was found that the traditional approach of preparing standard curves was somewhat in error because the simple addition of water to the extraction process produced some colouration in the methylene chloride, despite drying the extract. This results in inflated effectiveness values.

Experiments comparing correct chromatographic methods and colorimetric methods showed that the latter could yield errors as much as 300 o/oo. More typical medium oils showed errors of only a few percent, but heavy oils again showed significant error because of the different wavelengths at which they are absorbed. Gas chromatography is the only accurate means to analyze for dispersant effectiveness. Many values from effectiveness tests conducted in the past using colorimetric methods are questionable. For this reason, the data relating salinity and effectiveness are separated into those obtained by colorimetric and chromatographic methodologies. All literature surveyed in Sections 3 and 4 is summarized in Table 1. It should be noted that much of the older literature reported data in graph form and not in tables. The numeric data was estimated from the graphs and subsequently re-plotted.

Belk et al. (1989) studied the effectiveness of dispersants in the Labofina laboratory apparatus. They tested several dispersants at a range of salinities and found that all dispersants were less effective at lower salinities. Belk et al. also tested freshwater dispersants and found that these showed similar behaviour and were less effective at lower salinity. These researchers also found that the ionic strength and the type of ion changed the effectiveness of freshwater dispersants. The data for several oils are given in Table 2 and re-plotted as shown in Figure 1. The dispersants tested are not named but are noted alphabetically.

Most of the dispersants show the same tendency, that is the effectiveness decreases to low values near zero salinity. The dispersant tendency also decreases after achieving a maximum of about 20 to 25 degrees salinity. One dispersant, designated 'c', did not behave in quite the same manner, but the authors note that this dispersant is neither typical nor common. Although these data will be compared to recent data, the tendency is the same throughout the data reported in this paper. Figure 2 shows the data for freshwater dispersants. This shows that even the freshwater dispersants have low effectiveness at low salinities and peak at a salinity of about 10 o/oo.

Fingas et al. (1991) studied the effectiveness of dispersant-oil combinations under a variety of salinity conditions using the swirling flask test and colorimetric measurement. They found that the effectiveness peaked at between 40 to 45 o/oo and then dropped rapidly to low values. These data are given in Table 3 and illustrated in Figure 3. This is one of the few data sets to include salinities beyond about 40 o/oo.

3

Clayton et al. (1992, 1993) reviewed the effect of salinity in the literature and summarized many of the old data. Fritz (1995) also reviews these data. The first numeric results were by Wells and Harris (1979) who report a sharp effect in going from fresh to saltwater. The results are summarized in Table 4 and illustrated in Figure 4 (also includes data from Byford et al., 1983 and Lehtinen and Vesala, 1984). These older data generally show the same tendencies as described by other workers later, although the data are much noisier as would be expected. Byford et al. employed the Labofina test and Lehtinen, the Mackay test.

Brandvik and Daling (1992) and Brandvik et al. (1995) studied the effectiveness of dispersants at low temperatures and salinity for application in the Arctic. They used the IFP test and found that most dispersant-oil combinations showed a large decrease in effectiveness at lower salinities. One dispersant intended for use in freshwater, Inipol IPF, showed the opposite tendency. These data are given in Table 5 and shown in Figures 5 and 6. Most dispersant-oil combinations showed very low effectiveness at low salinities.

Fingas et al. (1994, 1995b) studied the effectiveness of dispersant-oil combinations under a variety of salinity conditions and produced a salinity curve similar to that noted above. They found that the effectiveness peaked at between 30 to 40 o/oo and then dropped rapidly to low values. These data are given in Table 6 and illustrated in Figures 7. This is a data set that again shows a decrease in effectiveness after a peak at about 30 o/oo.

MacKay (1995) reported on tests conducted at Exxon using the Exdet tests. Effectiveness was reported as staying constant, although rising somewhat from the salinity values of 5 through to 35 o/oo. The effectiveness was also reported to be very low in freshwater. These tests were done for Prudhoe Bay crude and Corexit 9527.

Moet et al. (1995) tested the effectiveness of Corexit 9527 on light Arabian crude over a series of salinities, using the Labofina or Warren Springs test. The salinity effect was the same as found by Fingas et al., 1992, 1994, 1995b. The effectiveness peaked at about 33 o/oo and then again decreased. These results are shown in Table 7 and illustrated in Figure 8. Moet's results show the same tendency as results from Fingas et al. (1992, 1994, 1995b) in that the effectiveness peaks at about a salinity of 30 o/oo and then falls rapidly as salinity increases.

George-Ares et al. (2001) tested the effectiveness of various dispersants in river water, distilled water, and water with calcium chloride added. The Exdet apparatus was used to carry out the tests. The lowest effectiveness was found in the distilled water and the effectiveness was higher in the river water. Adding calcium chloride to the dispersant increased the effectiveness above that of the river water. These results, as shown in Table 8, are generally consistent with those noted previously in that a decrease in effectiveness is noted with a decrease in salinity.

Guyomarch et al. (2002) tested the effect of dispersants and variables such as salinity on the aggregate formation with clay. They found that the aggregate particle size increased with increasing salinity.

4.   Recent Laboratory Testing

The effectiveness of dispersion at different temperatures and salinity has been measured using various tests. Blondina et al. (1997a, b) measured the effectiveness of dispersing Prudhoe Bay crude at 20°C and 20‰ as 23% for Corexit 9500 and 13% for Corexit 9527, using the EPA swirling flask method. The results also show that, for the same tests, the use of colorimetry as much as doubled the apparent effectiveness. It was concluded that the chromatographic method showed less bias to oils as dependant on their compositions. The results are shown in Table 9 and illustrated in Figure 9. These results are consistent with previously measured results noted in Section 3, namely that dispersant effectiveness is less with lower salinity.

Blondina et al. (1999) also measured the effectiveness of the dispersants Corexit 9527 and Corexit 9500 on several oils. The results are summarized in Table 10 and illustrated in Figure 10 for Corexit 9500 and Figure 11 for Corexit 9527. Blondina and coworkers concluded that the interaction between the salinity of the receiving water and the ability of surfactant-based dispersants to enhance petroleum accommodation into the water column can be both oil- and dispersant-specific. They found that Corexit 9500 was more effective than Corexit 9527 on most oils at most salinities, but the opposite was true in some cases. Corexit 9500 maintained its effectiveness over a wider range of salinities. Blondina et al (1999) concluded that decisions should be made on a specific situation based on the oil, the dispersant, and the salinity of the receiving water.

Moles et al. (2001, 2002) conducted a series of measurements on Alaska North Slope (ANS) oil at lower temperatures and lower salinity. For Corexit 9500 at a temperature of 10°C and 22 °/oo, the effectiveness was 8% for fresh ANS and 2% for weathered ANS. Under the same conditions, Corexit 9527 showed an effectiveness of 10% for the fresh ANS and 5% for the weathered ANS. The effectiveness of Corexit 9500 and Corexit 9527 was tested on Alaska North Slope crude oil at various salinities and temperatures representative of conditions found in Southern Alaskan waters. The oil was weathered to different degrees. Tests were conducted in a swirling flask at temperatures of 3, 10, and 22°C with salinities of 22 and 32 °/oo. Analysis was by GC. The authors concluded that, at the common temperatures found in the estuaries and marine waters of Alaska, the dispersants were largely ineffective. They also found that there was an interactive effect between temperature and salinity. A high effectiveness for 'emulsion', an uncharacterized mixture of oil and water, was attributed to 'osmotic shock' because of the difference in the salinity of the preparation (33 °/oo) and the test salinity. At the combinations of temperature and salinity such as might be typical for Alaska, dispersant effectiveness in the test was less than 10%. The results are summarized in Table 11. The data for the fresh ANS are plotted in Figure 12 for Corexit 9527 and in Figure 13 for Corexit 9500. Both figures generally show the decrease in effectiveness with decreasing salinity. There may be a relationship between temperature, salinity, and effectiveness as shown in these data.

The Moles data (Moles et al., 2001, 2002) were tested for ability to form a consistent relationship between temperature and salinity. This was carried out by correlating the three-dimension factors of effectiveness, salinity, and temperature. The results show that there is a high correlation for the fresh ANS and less so for the weathered and emulsified products. Table 12 shows the three-dimensional linear equation used to identify correlation. This shows that there is a good correlation between all factors, less so for the weathered and emulsified oils. A simple linear

5

equation is good for the fresh oil case but poor for the weathered and emulsified cases. Figures 14 to 17 show the linear correlations for the six oils. These figures show the three-way correlations as a plane surface or surface of best fit. Individual values are shown as circles and line extensions indicate whether these values are above or below the plane of best fit. It is important to note that such correlation as attempted here would be most valid if there were more data points.

Fingas et al. (2003) studied the effect of resurfacing of dispersed oil. As part of this study, a series of standard tests were conducted with Alberta Sweet Mixed Blend (ASMB) and Alaska North Slope (ANS) crude oils and the dispersants Corexit 9527 and Corexit 9500. Results are shown in Table 13 and illustrated in Figure 18. The same tendencies as Moles et al. (2001, 2002) found for ANS were found in this study, namely that the effectiveness of Corexit 9500 with ANS increases as salinity increases and that of Corexit 9527 generally does as well, but this is variable. The effectiveness of Corexit 9527 appears to peak at a salinity of 25 o/oo. It is not yet known why ANS has shown this tendency in these studies. The ASMB and most other crudes shows the tendency throughout this study that the effectiveness is Gaussian with the peak in this case coming at about 20 o/oo.

Sterling et al. (2004) studied the coalescence of dispersed oil droplets. Theoretical studies were conducted using DLVO theory and kinetic studies were conducted using a laboratory apparatus. Sterling et al. came to the following conclusions.

1. For salinity and pH values found in natural waters, the ζ- potential values of chemical dispersed crude oil were slightly negative. The ζ- potential is a measure of charge between particles and is relevant to dispersants in that a higher ζ- potential indicates a more stable particle and could imply a higher effectiveness. For a fixed pH value, ζ- potential values become marginally more negative with increased water salinity. This is shown in Figure 19. Using DLVO theory, no significant electrostatic energy barrier to droplet coalescence was present. This implies that oil dispersions (including those with dispersants) are unstable over time.

2. Within the tested experimental conditions, the collision efficiency parameter, α, (the probability of successful particle-particle collision) was significantly greater than 0. This result suggests that coalescence kinetics were important in estimating dispersant efficiency in laboratory-scale protocols and may be important in coastal spills. This is shown in Figure 20. The shear rate was the dominant parameter in estimating observed coalescence rates and dispersant efficiencies. This implies that the effectiveness is very dependent on shear rate, but that the resulting emulsions will also be unstable and in fact coalescence occurs faster under some energetic conditions.

3. Salinity had a limited influence on effectiveness values measured in this study. Sterling et al. suggest that salinity has a strong overall effect and thus, because salinity shows a lesser effect on coalescence, that salinity must have a greater effect on initial droplet formation.

6

5.   Salinity Effects in Surfactant Literature

A literature search was conducted of the body of literature on surface chemistry. This search focussed on the effects of salinity on various aspects involving the use of surfactants. The papers are summarized in Table 14 and, where available, numeric results are given in Table 15. The values in Table 15 are given in terms of relative values compared to the value at 0 o/oo.

Davis (1994) reviews the basic surfactant chemistry and physics. He notes that interfacial tension of an oil-water system varies widely with salinity and is generally at a minimum at 15 ppt for many surfactant systems. Davis also provides information on the typical phase changes with changing salinity, including the effects of alkane change length and water fraction. Ysambertt et al. (1997) describes the phase behaviour of emulsions noting that salinity was an important factor in describing phases.

Several authors have studied oil recovery and the effectiveness of surfactants with respect to the salinity of the pore water. Sayyouh et al. (1993) studied the effect of salinity on a surfactant-oil-brine system and found that the stability of the system increased up to the salinity of about 3.8o/oo and then decreased as the salinity rose to 23o/oo . Fjelde and Austad (1994) studied the analysis of salt-tolerant and non-salt-tolerant surfactants, noting that ethoxylated anionic surfactants can tolerate high salinity water. These types of surfactants are not used in oil spill dispersants.

 Several authors have tested oil reservoir recovery chemicals and found that increasing salinity increases performance of these surfactants (Austad et al., 1994; Fjelde et al., 1995; Austad and Strand, 1996. Wu et al. (2004) developed a new performance index for surfactants named the relative solubility index. This was used to examine a series of different surfactants at various salinities for oil recovery applications. Drummond and Israelachvili (2002) studied the fundamentals of surface forces and wettability, noting that recovery would be improved with increases in salinity. They also noted that recovery via natural surfactants is improved in high saline waters. Babadagli (2003) found that increasing salinity increased recovery with and without a surfactant. Zhang et al. (2004) studied natural surfactants and found that the recovery from reservoirs was increased with increasing salinity. Liu et al. (2004) studied the effectiveness of oil recovery and noted that increasing salinity increased the partition of surfactant into water. Al-Roomi et al. (2004) studied the use of surfactants to improve the flow properties of oil. Surfactants are used to emulsify oil into the water. Al-Roomi and co-workers found that the dispersion and viscosity reduction improved as surfactant content increased.

Several authors studied the effect of salinity on oil or specific hydrocarbons. Song and Islam (1994) studied the use of surfactant washing for cleaning petroleum from soil. They found that increasing salinity increased the removal or the effectiveness of the surfactant. Watt et al. (1998) studied the formation of a water-in-oil emulsion with a cationic surfactant and diesel oil. They found that the formation tendency increased with salinity up to about 30o/oo salinity and then decreased. Li and Chen (2002) studied the solubilization of PAHs into water with surfactants and found that increasing salinity decreased the cloud point, increased the apparent solubility, and reduced the hydrodynamic radius. Li and Kunieda (2003) studied the effect of having a cationic and an anionic surfactant to dissolve oil and found that salinity increased the effectiveness of the surfactants. Ghannam and Chaalal (2003) tested a vacuum oil recovery system which also used

the surfactant Triton X-100. They found that increasing salinity greatly increased recovery. Moosai and Dawe (2003) studied the theoretical aspects of the use of gas flotation for oily wastewater cleanup. They noted that the flotation improves with salinity and surfactant amount. Chen et al. (2004) studied the change in interfacial tension between hexane and an ionic surfactant. The interfacial tension decreased sharply with a small amount of salinity and rose again slightly and peaked at about 10 ppt. Mollet et al. (1996) also studied interfacial tension but with paraffin oil and sodium linoleate and an in-situ formed surfactant. They found that the optimal IFT occurred with salinities between 10 and 30 ppt.

Some authors studied the solubilization of specific compounds. Chooro et al. (1996) studied the miscellization and adsorption of a zwitterionic surfactant, n-dodecyl betaine, with salt concentrations. These researchers found that the adsorption of the surfactant onto silica gel depended little on temperature, but very much on the salt concentration. Yu et al. (2004) studied the extraction of a bacterial toxin from water using a cationic surfactant. They found that increasing salinity increased the partition of the water portion of the extract. Park and Bielefeldt (2003) studied the partitioning of pentachorophenol into a mineral oil with varying amounts of a nonionic surfactant and found that a higher ionic strength increased the partitioning.

The effects on physical systems of surfactants and varying salinity were investigated by various authors. Abuin et al. (1993) studied the formation of microemulsions with ionic surfactants and found that stability increased with salinity for most CTAC surfactants and decreased if CTAB was the majority surfactant. Hou and Papadopoulis (1996, 1997) studied three-way emulsion droplets and found that the stability of these droplets with surfactant increased significantly with increasing salinity. Kaczmarski et al. (1999) studied the influences of surfactant and salinity on the viscosity of a polymer thickness. The viscosity of the thickener decreased with increasing salinity.

Kjøniksen et al. (1999) studied the formation of gels of ethyl (hydroxyethyl) cellulose with the surfactant sodium dodecyl sulphate (SDS) and found that the intermolecular structure of the gel is increased with increasing salinity. Prosser and Franses (2003) used a thermodynamic/electrostatic model to study sodium dodecyl sulfate/sulfonate systems. They concluded that salinity increases stability by lowering interfacial tension. Sabatini et al. (2003) studied the effect of linker molecules with surfactants in solubilization. They found that solubilization with naphthalenic sulfonates was very saline-dependent and governed the solubility/surfactant concentration relationship.

8

6.   Field Studies and Effects Studies

Some studies focussed on examining the effects of oil dispersed into the freshwater environment. Scott et al. (1979) studied the effects of a freshwater dispersal into a pond. The authors noted that there were significant similarities between the dispersed oil and the non-dispersed oil. The dispersed oil remained in a 3 to 5 cm milky layer only for about an hour after which it separated and formed a slick similar to that of the oil-only pond. This indicates a relatively poor dispersant effectiveness.

Brown and Goodman (1989) report on an extensive study of the effects of oil in the freshwater environment. Several toxicity and behavioural tests are described, but these are not compared to similar species in the saltwater environment. Brown et al. (1990) describe a major field trial of dispersants in the freshwater environment. Three cubic metres of Norman Wells crude oil were spilled on each of two fen lakes. The slick on one lake was treated with the dispersant Corexit 9500. The workers claimed that the dispersant was effective at removing oil from the surface of the one lake but also reported the appearance of thick clumps of oil near the edge of the same pond. The impact of the oil on the fen appeared to be lessened by the use of the dispersant, gauged primarily by the impact on floating vegetation. After one month, there was little impact on either fen. This study concluded that the best response to a spill in such a lake was no response at all.

Clayton et al. (1989) studied chemical and mechanical dispersion in an artificial stream bed. They concluded that the value of added dispersant was tempered by various factors including viscosity of the oil, degree of exposure of sediment surfaces to the oil, sediment substrate characteristics, and water flow characteristics.

Wolfe et al. (1998) studied the uptake of naphthalene by an algae. The oil was Prudhoe Bay crude and the dispersant was Corexit 9527. It was found that the dispersant significantly affected the uptake of naphthalene (by as much as 50%). Salinity, however, did not affect this uptake significantly. The results are shown in Table 16 and Figures 21 and 22. These data show that the uptake of naphthalene and a,b naphthol sulphate are relatively unaffected by salinity. Wolfe et al. (1999) also studied the heat shock protein in *Isochrysis galbana*, a golden-brown algae and primary producer in marine food chains. Wolfe et al. found that the organism efficiently induced the heat shock protein hsp60 in response to elevated temperatures and exposure to low concentrations of petroleum hydrocarbons after a model oil spill and dispersant use. Differences in salinity were found to influence the induction of hsp60 by elevated temperature, WAF and DO preparations, and naphthalene. Increased salinity appeared to decrease the sensitivity of *I. Galbana* to hsp60 induction after exposure to these agents. They suggest that the hsp60 induction may serve as an adaptive function in *I. Galbana* to deal with exposures to oil and dispersants. This also suggests that dispersants/oil may be more toxic at low salinities.

7.   Salinity in Prince William Sound

The waters in Prince William Sound vary in salinity (Vaughn et al., 2001; Gay and Vaughn, 2001; Bang and Mooers, 2003). The data generally indicate that the salinity in the middle of the Sound is about 33 o/oo. As one enters areas influenced strongly by river outfalls, however, the salinity drops to that of freshwater. While the range of salinities in the Sound certainly raises concern, the salinity is generally higher than 20 o/oo in the centre of the sound where dispersants are likely to be used.

Figure 23 shows Prince William Sound and the detailed sampling stations. Figure 24 shows varying salinities at the Zaikof Bay station. This figure shows that surface salinities often are 28 o/oo and range only as high as 31.5. This is typical of most of the central portion of the Sound. Figure 25, on the other hand, shows the salinity profiles at Eaglek Bay. The water salinity in this area, which is typical of most of the fringe regions of Prince William Sound, ranges from 20 to 31.5 o/oo. A similar profile is seen in the Whale Bay data as shown in Figure 26. Table 17 shows recent salinity testing results. This data, from Tony Parkin, shows that the outfalls of creeks are very low in salinity. The smaller bays are also very low in salinity. Dispersant application should not be considered in or near such regions where salinity is below 20 o/oo. It must be noted however that salinity varies very much with season and location.

In Alaska, there are three distinct dispersant use zones (Annex I to the Alaska: RRT Dispersant Use Guidelines for Alaska). Zone 1 delineates an area where dispersant use has been preapproved. The On-Scene Coordinator (OSC) is not required to consult with any other agencies prior to the use of dispersants in this zone. In Zone 2, dispersant use can be approved by the OSC, but only with the concurrent approvals from the Environmental Protection Agency (EPA) and the State of Alaska. The use of dispersants is not recommended in a Zone 3 but can be used on a case-by-case basis. Prior to use in a Zone 3, the OSC is required to consult with the Regional Response Team and obtain approvals from the EPA and the State of Alaska.

Generally, Zone 1 in Prince William Sound runs through the center and entrance of the Sound, what is commonly referred to as the "tanker lane." Zone 1 also runs along the southern edge of the entrance to the Sound. The Gulf of Alaska is a Zone 2. Much of the Eastern and Western areas are a Zone 3. Port Valdez is unique in that it has seasonal designations, that change it from a Zone 1 to a Zone 2 depending upon the season, although the eastern edge of the Port is always a Zone 3.

Alaska is unique in the United States in that it has a preapproval zones so close to the nearshore. Many of the preapproval zones in the other states are beyond three nautical miles. This is of concern with respect to salinity, as many of these pre-approval zones are in low salinity zones and the effectiveness of dispersants would be very low in these areas.

8.   Summary

Surfactants are the active ingredient in dispersants. Surfactants work to sustain oil droplets in the water by maintaining a portion of the molecule in the oil (lipophilic) and in the water (hydrophilic). The ratio of lipophilic to hydrophilic depends on the ionic strength of the water which relates directly to the salinity. The hydrophilic portion of the surfactant is more

soluble in water with a higher salinity. As salinity rises past a certain point, the surfactant becomes too soluble in the water and has a stronger tendency to partition to the water phase completely. Thus, in theory, the surfactant is more lipophilic in freshwater and increases in hydrophilicity as the salinity rises. The stability of the resulting droplets also depends on salinity due to the increasing ionic strength of the water as salinity rises. This increasing ionic strength results in greater molecular force. Again, as the salinity rises above a certain point, this point being dependent on the particular type of surfactant, this increased force results in more surfactant molecules leaving the oil drop entirely.

There is a theoretical scale of hydrophilic/lipophilic balance or HLB. This is calculated by the type of surfactant present. A surfactant with an HLB of 10 is a dispersant, that is the force of the molecule is equally balanced between hydrophilic and lipophilic tendencies. A surfactant of much greater than 10 is said to form oil-in-water emulsions (dispersions) and one of much lower than 10 can promote the formation of water-in-oil emulsions. The HLB of a surfactant changes with salinity. A low salinity lowers the HLB and vice versa. Thus, it is theoretically possible to design a dispersant with surfactants for lower salinity waters. While this possibility exists, it should be noted that the stability of dispersions is less in less saline waters. Furthermore, it should be noted that there are no recent measurements on freshwater dispersants, indicating that the industry has not pursued this avenue.

This report reviews several older dispersant tests beginning at 1979. These were separated from more recent data because both testing procedures and analytical methods used at that time are not as accurate as today's methods. Some older methods may, in fact, not yield data with sufficient accuracy to discriminate salinity effects. However, for the most part, this review shows that the older data, with a few exceptions, are entirely consistent in the generic conclusions of modern data, while not consistent in the actual numbers.

The following are the findings of several workers.
  a) In waters with a salinity of 0 o/oo, most dispersants have a very low effectiveness or are sometimes even completely ineffective.
  b) Dispersant effectiveness peaks in water with a salinity from 20 to 40 o/oo.
  c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and as it exceeds this value.
  d) Some early works showed data anomalies, which may have resulted from measurement limitations and difficulties.
  e) Studies published earlier than about 1989 are not highly accurate and contain the most anomalies.

Newer testing is also reviewed in this report. This testing is marked by the use of chromatography for analysis and the use of very strict protocols in operating the dispersant tests. These tests are marked by having standard deviations of less that 10% and often less than 5%. These are less than an order-of-magnitude of standard deviations in previous testing.

The followings are the conclusions of the authors of these newer studies.
  a) In waters with a salinity of 0 o/oo, most dispersants have a very low effectiveness or are sometimes even completely ineffective.
  b) Dispersant effectiveness peaks in water with a salinity from 20 to 40 o/oo. This may depend on the type of dispersant used. Corexit 9500 appears to be less sensitive to salinity, but

11

still peaks at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and at about 35 o/oo with others.

c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and as it exceeds this value. The curves for this salinity appear to be Gaussian as shown in Figures 3, 7, and 8.

d) While there is some evidence for a temperature-salinity interaction as noted in the data of Moles et al., 2002, there is not enough data to make solid conclusions.

e) Recent data are almost exclusively measured using Corexit 9527 and Corexit 9500 and, since these have the same surfactant packages, there is a concern that the results may be more relevant to these formulations than to all possible formulations.

f) The values found in recent tests are much lower than the older tests, however, the trends are the same.

The general surfactant literature was reviewed for salinity effects on surfactants and surfactant phenomena. There is a body of literature on the use of surfactants for secondary oil recovery. There are several commonalities among the many findings. Recovery efficiency falls off at both high and low salinities. The salinity at which surfactant efficiency peaks is very dependent on the structure of the specific surfactant.

Several studies on the interaction of specific hydrocarbons and surfactants were reviewed. The consensus of these papers is that the solubility of the hydrocarbon increases with increasing salinity and decreases at low salinities. The interfacial tension of water and oil changes with surfactant and salinity. The interfacial tension is higher at lower salinities. The optimal interfacial tension is generally achieved at salinities of between 25 to 35 o/oo.

A number of physical systems involving surfactants and salinity changes are reported in the literature. Included in these is the finding that the stability of microemulsions is greater at salinities of 25 to 35 o/oo. Some workers found that the stability of systems was very low in fresh water or waters of salinities of < 10 o/oo. Similar effects were found with gels, polymer thickeners, and linker-molecule solubilization.

Some field studies of dispersant application were conducted in the freshwater environment. While effectiveness was not specifically measured, it was noted in both series of studies that effectiveness may have been low. In the one study, the investigators noted that the surfactants had poor effectiveness and stability. In this particular case, the dispersion lasted only about an hour and the dispersion was limited to a few centimetres. In another case, it was noted that in the dispersed pond, there was oil around the edges within a short time of dispersant application. Effects were monitored in both cases, but could not be compared and were not compared to similar applications at sea.

Some effects studies were conducted under varying salinity conditions. In one study, naphthalene and a,b napthol sulphate uptake were studied under different salinity conditions. There were no significant differences for different salinities, although naphthalene uptake was somewhat higher under low salinity conditions. Another study examined the induction of hsp60 protein in golden-brown algae. It was found that greater salinity reduced the effects of the simulated oil spills to the algae.

The salinity of the water in different parts of Prince William Sound was summarized. There are

12

areas of low salinity where dispersant application would result in reduced dispersant effectiveness.

9. Conclusions

The following are the overall conclusions of this study.

a) In waters with a salinity of 0 o/oo, conventional and currently available dispersants have a very low effectiveness or are sometimes even completely ineffective. This is consistent with physical studies in the surfactant literature.

b) Dispersant effectiveness peaks in waters with a salinity ranging from 20 to 40 o/oo. This may depend on the type of dispersant. Corexit 9500 appears to be less sensitive to salinity, but still peaks at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and at about 35 o/oo with others.

c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and after it exceeds this value. The curves for this salinity effect appear to be Gaussian.

d) While there is some evidence for a temperature-salinity interaction as noted in the data of Moles et al., 2002, there is not enough data to make solid conclusions.

e) Recent data are almost exclusively measured using Corexit 9527 and Corexit 9500. Since these have the same surfactant packages, there is a concern that the results may be more relevant to these formulations than to all possible formulations.

f) Observations on two field trials in freshwater appear to indicate that the laboratory tests are correct in concluding very low dispersant effectiveness in freshwater.

g) There were few studies on the biological effects of varying salinity and given oil exposure. There are not sufficient data to reach conclusions.

h) The findings in the dispersant literature reviewed here are in agreement with those in the theoretical and basic surfactant literature. The effect of ionic strength and salinity on both hydrophilic-lipophilic balance and stability is the reason for the decreased effectiveness noted at low salinities and the same decrease at high salinities above a certain peak of about 20 to 40 o/oo.

i) The waters of Prince William Sound are sometimes low in salinity, often less than 15 o/oo, especially near river outfalls. This could result in lower dispersant effectiveness.

Table 1   Summary of Testing of Salinity Effects on Dispersant Effectiveness

Author	Year	Dispersant Type (s)	Specific Surfactant	Type of Test	Generic Results
Wells and Harris	1979	Commercial	Corexit 9527	Mackay	Effectiveness decreased very much from saltwater to freshwater.
Byford et al.	1983	Commercial	Several commercial dispersants	Labofina effectiveness	Saltwater and freshwater dispersants decreased in effectiveness going down to zero salinity and decreased after 20 o/oo.
Lehtinen and Vesala	1984	Commercial	Two unidentified dispersants	Mackay	Decreased in effectiveness going down to low salinity.
Belk et al.	1989	Several	Designated A to F, both saltwater and freshwater dispersants	Labofina effectiveness	Saltwater and freshwater dispersants decreased in effectiveness going down to zero salinity and decreased after 20 o/oo.
Fingas et al.	1991	Commercial	Corexit 9527 & Enersperse 700	Swirling Flask	Commercial dispersants decreased in effectiveness going down to zero salinity and decreased after about 35 o/oo.
Brandvik and Daling	1992	Several	Several commercial dispersants	IFP	Saltwater and freshwater dispersants decreased in effectiveness going down to 5 0.00 salinity and decreased after 20 o/oo. One Labofina product showed opposite tendency.
Fingas et al.	1994, 95b	Commercial	Corexit 9527 & Enersperse 700	Swirling Flask	Commercial dispersants decreased in effectiveness going down to zero salinity and decreased after about 33 o/oo.
Brandvik et al.	1995	Several	Several commercial dispersants	IFP	Saltwater and freshwater dispersants decreased in effectiveness going down to 5 0.00 salinity and decreased after 20 o/oo. One Labofina product showed opposite
Moet et al.	1995	Commercial	Corexit 9527	Labofina effectiveness	Commercial dispersant decreased in effectiveness going down to zero salinity and decreased after about 33 o/oo.
Mackay	1995	Commercial	Corexit 9527	Exdet	Effectiveness in distilled water was very low but didn't change much after salinity increased past 5 o/oo.
Blondina et al.	1997 a,b	Commercial	Corexit 9527 and Corexit 9500	Swirling Flask	Effectiveness increased from salinity of 10 up to salinity of 30 for Corexit 9500 and up to 20 o/oo and then decreased otherwise.
George-Ares et al.	2001	Commercial	Corexit 9500 Enersperse 1037 Dasic Freshwater hipol PF	Exdet	Effectiveness in distilled water could be improved by the addition of calcium chloride.
Moles et al.	2001	Commercial	Corexit 9527	Swirling Flask	Effectiveness increased from salinity of 10 up to salinity of 30 for Corexit 9500 and up to 20 o/oo and then decreased otherwise.
Guyomarch et al.	2002	Commercial	hipol IP90	Special - 250 mL beaker	The aggregate size of particles increased with salinity.
Fingas et al.	2003	Commercial	Corexit 9527 and Corexit 9500	Swirling Flask	Effectiveness increased from salinity of 10 up to salinity of 30 for Corexit 9500 and up to 20 o/oo and then decreased otherwise.

14

Table 2 Data from Belk et al. (1989)

Actual Values Taken from Graph

Effectivness for Warren Spring Oil at 10°C | | | | | **Effectivness for Prudhoe Bay Oil at 10°C**

Salinity	Disp A	Disp B	Disp C	Disp D	Salinity	Disp A	Disp B	Disp C	Disp D
0	5	5	25	5	0	10	4	35	3
5	10	8	23	10	5	25	12	27	7
10	23	20	22	23	10	42	27	22	15
15	60	55	25	25	15	57	36	22	22
20	75	65	35	35	20	62	42	25	27
25	77	67	47	47	25	57	37	28	35
30	80	70	55	58	30	55	32	35	45
35	82	72	60	60	35	42	25	37	52

Effectivness for Warren Spring Oil at 20°C | | | | | **Effectivness for Prudhoe Bay Oil at 20°C**

Salinity	Disp A	Disp B	Disp C	Disp D	Salinity	Disp A	Disp B	Disp C	Disp D
0	0	0	37	2	0	12	6	32	3
5	17	11	23	3	5	26	17	23	6
10	32	23	18	5	10	42	28	22	14
15	47	32	20	10	15	55	40	24	20
20	57	42	23	17	20	60	45	25	25
25	65	46	27	27	25	58	42	30	32
30	70	50	35	40	30	50	40	34	37
35	72	52	43	47	35	40	32	37	41

Effectivness for Warren Spring Oil at 10°C *Freshwater* | **Effectivness for Warren Spring Oil at 20°C** *Freshwater dispersants*

Salinity	Disp E	Disp F			Salinity	Disp E	Disp F
0	62	25			0	55	32
5	77	47			5	67	60
10	85	62			10	74	74
15	84	67			15	75	80
20	82	72			20	73	80
25	77	74			25	67	77
30	75	72			30	60	75
35	72	70			35	50	70

Effectivness for Prudhoe Bay Oil at 10°C *Freshwater* | **Effectivness for Prudhoe Bay Oil at 20°C** *Freshwater dispersants*

Salinity	Disp E	Disp F			Salinity	Disp E	Disp F
0	25	24			0	24	23
5	45	44			5	44	43
10	58	56			10	56	54
15	64	62			15	68	65
20	62	60			20	70	68
25	58	56			25	68	66
30	56	54			30	66	64
35	42	44			35	56	54

Ionic Strength Effects for Dispersant E | | | **Ionic Strength Effects for Dispersant F**

Ionic strength mol l-1	Mg	Ca	Ionic strength mol l-1	Mg	Ca
0.05	40	64	0.05	72	72
0.1	50	68	0.1	76	66
0.2	65	70	0.2	78	60
0.3	80	72	0.3	79	56
0.4	85	72	0.4	76	56
0.5	80	68	0.5	72	58
0.6	72	56	0.6	60	62

15

Table 3   Dispersant Effectiveness Data from Fingas et al., 1991

Salinity o/oo	ASMB Corexit	ASMB Enersperse	Norman Wells Enersperse	Adgo Corexit
0	0	0	0	0
10	8	8	3	14
20	12	11	11	28
30	25	41	30	42
35	30	55	40	43
40	38	68	48	44
50	39	73	39	35
60	41	13	12	33
70	32	6	7	23
80	12	5	5	16
90	9	2	2	7

Table 4   Results of Older Salinity Testing

Oil and Temperature	Dispersant	Effectiveness % at a given salinity Salinity o/oo				
Data from Byford et al., 1983		**0**	**5**	**10**	**22**	**33**
Lago Medio Residue 0°C	Arochem D609	8		11	18	25
	Corexit 9527	10	12	18	30	35
North Slope Crude 0°C	Arochem D609	12	30	34	46	51
	Corexit 9527	12	35		48	52
North Slope Residue 0°C	Corexit 9550	22	61	62	52	50
	Dispolene 34S	15	60	62	58	62
	Finasol OSR5	15	17	20	19	21
	Corexit 9527	25	29	25	26	27
	Experimental	78	70	68	70	79
Data from Lehtinen and Vesala, 1984		**3**	**7**	**12**		
Fresh Russian Crude 15°C	A	60	62	65		
	B	60	55	62		
	C	45	40	47		
Fresh Russian Crude 4°C	A	20	21	30		
	B	10	8	9		
	C	10	12	9		

16

Table 5   **Results of Salinity Testing from Brandvik and Daling, 1992**

Oil and Temperature	Dispersant	Effectiveness at Given Salinity %		Oil and Temperature	Dispersant		
		33 o/oo	5 o/oo			33 o/oo	5 o/oo
Oseberg 0°C	Dasic NS	80	5	IFO 0°C	Enersperse 700	67	48
	IKU-9	78	10	Weathered	Inipol IPC	42	37
	Inipol IPC	76	48		OSR 52	58	54
	E-700	76	55		Dasic Freshwater	37	38
	Dasic LTS	62	12		Inipol IPF	25	45
	E-1075	59	55	Veslefrikk 0°C	Enersperse 700	58	54
	Dasic Freshwater	38	45	w/o	Inipol IPC	80	40
	Corexit 9527	36	5		OSR 52	10	15
	Disp. 365	30	7		Dasic Freshwater	30	8
	Corexit 9550	29	20		Inipol IPF	8	60
	OSR 52	26	28	Oseberg 0°C	Enersperse 700	68	58
	Inipol IPF	24	50	w/o	Inipol IPC	68	44
	Disp. 385	20	24		OSR 52	25	35
	OSR 5	15	4		Dasic Freshwater	30	35
Oseberg 0°C	Enersperse 700	70	69		Inipol IPF	20	50
Weathered	Inipol IPC	68	40	IFO 0°C	Enersperse 700	30	4
	OSR 52	20	65	w/o	Inipol IPC	50	4
	Dasic Freshwater	25	23		OSR 52	30	4
	Inipol IPF	18	70		Dasic Freshwater	24	10
Oseberg 0°C	Enersperse 700	82	55		Inipol IPF	36	28
Weathered 2	Inipol IPC	86	30				
	OSR 52	80	30				
	Dasic Freshwater	65	58				
	Inipol IPF	25	70				

Dispersant	Salinity	Effectiveness
IPF Inipol	0.5	38
	1.25	58
	2	78
	2.75	80
	3.5	70
IPC Inipol	0.5	85
	1.25	80
	2	25
	2.75	21
	3.5	18

17

Table 6   Dispersant Effectiveness Data from Fingas et al., 1994, 1995b

Salinity o/oo	ASMB Corexit 9527	ASMB Enersperse	Norman Wells Enersperse 700	Adgo Corexit
10	8	9	4	14
20	12	11	11	29
30	25	41	31	42
33	32	57	35	39
40	38	68	48	44
50	39	73	39	36
60	41	13	12	35
70	32	6	7	24
80	12	5	5	16
90	10	3	2	6

Table 7   Data from Moet et al., 1995

Salinity	Effectiveness (%)
0	3
20	6
30	16
33	14
40	7
50	3

Table 8	Data from George-Ares et al., 2001					
		Effectiveness in Percent				
Crude Oil	Water	Corexit 9500	Corexit 9500 + Salt	Dasic Freshwater	Enersperse 1037	Inipol IPF
Hydra	Rio de la Plata	49	56,70	71	68	58
	Deionized	32	58	70	70,64	65
Escalante	Rio de la Plata	2	17	27	19	
	Deionized	<5	11 to 22	27	16	7
Canadon Deco	Rio de la Plata	21	25	34	36	
	Deionized	10	42,40	56	37	17

18

Table 9 **Dispersant Effectiveness Measured by Blondina et al., 1997a, b**

Effectiveness in % at given salinity

Oil Type Prudhoe Bay	Salinity (o/oo) 35	30	25	20	15	10
Corexit 9500	23	21	22	23	15	12
Corexit 9527	34	29	13	13	9	5

Table 10 **Dispersant Effectiveness Measured by Blondina et al., 1999**

Corexit 9500 — Effectiveness in % at given salinity

Oil Type	35	30	25	20	15	10	5	0
Arabian Light	38	36	44		31		7	
Arabian Medium	20	24	26	24	11	10		
Forcados	21	31	35	37		26		6
Kuwait	37	38	31		15		5	
Maya	16	11	12		6		3	
Oman	22	20	15		10		3	
Prudhoe Bay	23	21	22	23	15	12		

Corexit 9527 — Effectiveness in % at given salinity

Oil Type	35	30	25	20	15	10	0
Arabian Light	23	13	10		6		
Arabian Medium	10	5	7	6	6	3	
Forcados	54	63	55	48		17	6
Kuwait	21	13	7				
Maya	5	4					
Oman	7	5	6				
Prudhoe Bay	34	29	13	13	9	5	

19

Table 11 Data from Moles et al., 2001, 2002

Oil Type	Temperature	Corexit 9527		Corexit 9500	
		Effectiveness in percent			
		Salinity		Salinity	
	°C	22 °/oo	32 °/oo	22 °/oo	32 °/oo
Fresh ANS	3	8.5	1	10	10
	10	7.9	15	10	22
	22	35	31	16	18
20% evap. ANS	3	6.3	6.5	6.3	6.3
	10	1.7	4.1	4.5	2.6
	22	6.3	6.3	6.3	6.3
emulsified' ANS	3	26	20	13	23
	10	73	32	42	29
	22	17	20	24	14

Table 12 Prediction of Temperature and Salinity Interrelationship (Data from Moles et al., 2001, 2002)

Equation: Effectiveness = a + b*temperature + c*salinity

Dispersant	Oil	a	b	c	Linear r	Best r_2
9527	fresh ANS	2.6	1.5	-0.15	0.92	0.94
9500	fresh ANS	-2.2	0.34	0.47	0.57	0.72
9527	weathered	2.6	0.026	0.09	0.07	0.85
9500	weathered	6.8	0.025	-0.06	0.07	0.85
9527	emulsion	77	-0.52	-0.15	0.19	0.61
9500	emulsion	37	-0.1	-0.43	0.06	0.68

20

Table 13 Salinity and Effectiveness (Data from Fingas et al., 2003)

Oil	Dispersant	Salinity	Effectiveness	Std. Dev
ASMB	Corexit 9500	5	21.9	3.4
ASMB	Corexit 9500	10	24.1	1.3
ASMB	Corexit 9500	20	52.8	1.3
ASMB	Corexit 9500	33	43.8	6.5
ASMB	Corexit 9527	5	24.1	2.1
ASMB	Corexit 9527	10	23.3	2.2
ASMB	Corexit 9527	20	54.2	5.5
ASMB	Corexit 9527	33	36.6	3.5
ANS	Corexit 9500	5	19.4	1.1
ANS	Corexit 9500	10	18.8	0.7
ANS	Corexit 9500	20	21.9	1.9
ANS	Corexit 9500	33	34.8	4.7
ANS	Corexit 9527	5	17.1	0.8
ANS	Corexit 9527	10	17.2	1.7
ANS	Corexit 9527	20	24.6	0.8
ANS	Corexit 9527	33	25.9	2.8

ASMB = Alberta Sweet Mixed Blend
ANS = Alaska North Slope Blend

21

Table 14   Summary of Authors and Findings from Surfactant Literature

Author	Year	Surfactant Type	Specific Surfactant	Type of Test	Generic Results
Abuin et al.	1993	Ionic	CTAB and CTAC	Microemulsion stabilization	Stabilization increases with salinity except for one surfactant
Al-Roomy et al.	2004				
Austad and Strand	1996	Ionic	Exxon RL-3011	Oil behaviour	Salinity has large effect
Austad et al.	2004				
Babadagli	2003	Nonionic	Oxyethanol ethyoxylate	Recovery from reservoir	Recovery increases with salinity
Chen et al.	2004	Ionic	CTAB	Interfacial tension	IFT decreases and then increases
Chooro et al.	1996	Zwitteronic	N-dodecyl Betaine	Relative solubility	RSD decreases with salinity
Davis	1994	Most		Reviews basics	IFT decreases with salinity
Drummond & Israelachvili	2002	Various		Surface forces	Surface forces decrease with salinity
Fjelde and Austad	1994				
Fjelde et al.	1995	Dual ionic	6EOS & DDBS	Recovery from reservoir	Recovery increases with salinity
Ghannam and Chaalal	2003	Nonionic	Triton X100	Oil spill recovery	Recovery increases with salinity
Hou and Papadopoulis	1996	Nonionic	Tween 80 & Span 80	Droplet stability	Drop stability increases with salinity
Hou and Papadopoulis	1997	Nonionic	Tween 80 & Span 80	Droplet stability	Drop stability increases with salinity
Kaczmarski et al.	1999	Dual ionic & nonionic	SDS & Triton 100	Thickener viscosity	Viscosity lower as salinity increases
Kjøniksen et al.	1999	Ionic	SDS	Gel structure	Salinity increases molecular associations
Li and Chen	2002	Nonionic	Tergitol 15-S-X, Triton X 100, Tween 20, Tween 80	Partitioning of org. into oil	Partitioning increases with salinity
Li and Kunieda	2003	Mixed	Anionic and cationic	Relative solubility	RSD decreases with salinity
Liu et al.	2004				
Mollet et al.	1996	Ionic	Sodium linoleate	Interfacial tension	IFT decreases and then increases
Moosai and Dawe	2003	Various	Various	Gas flotation	Wastewater cleanup improved with salinity
Park and Bielefeldt	2003	Nonionic	Tergitol NP-10	Partitioning of org. into oil	Partitioning increases with salinity
Prosser and Franses	2003	Ionic	SDS & SDSn	Model of IFT equilibrium	Salinity decreases IFT
Sabatini et al.	2003	Ionic	Naphthalene sulphonates	Solubilization	Very salinity-dependent
Sayyouh et al.	1993	Ionic	Sulphonates	Phase behaviour of oil-surfactant-brine	Stability increases up to 3.8% and then decreases as salinity goes to 23%
Song & Islam	1994				
Watt et al.	1998	Cationic	CTAB	Water-in-oil emulsion	Formation improves up to about 30% salinity
Wu et al.	2004	Nonionic	Brij 30	Relative solubility	RSD decreases with salinity
Wu et al.	2004	Nonionic	Tween 20	Relative solubility	RSD decreases with salinity
Wu et al.	2004	Nonionic	Igepol CO210	Relative solubility	RSD decreases with salinity
Ysambertt et al.	1997	Most		Reviews basics	Wins or states affected by salinity
Yu et al.	2004	Cationic	Aliquat-336	Extraction effectiveness	Extraction increases with salinity
Zhang et al.	2004	Natural	Acid fractions	Recovery from reservoir	Recovery increases with salinity

22

Table 15 Quantitativ e Data on Salinity Change from Surfactant Literature

(all data converted to relative effectiveness compared to 0 salinity)

Author and Details	Salinity o/oo	Increase in Effect (from 0)	Change in Solubilty	Reduction in IFT	Notes
Wu et al., 2004 nonionic	50		4.1		
	100		5.8		
	50		2.7		
	100		3		
	50		3.4		
	100		5.2		
Chen et al., 2004 ionic	1			99.7	
	2			99.4	
	5			99.3	
	7			99.2	
	9			99.1	
	11			99.2	
	15			99.6	
Mollet et al., 1996	5			22	
	10			44	
	20			38	
	30			35	
Kaczmarski et al., 1999	20	64			surf = .01
	30	84			surf = .01
	20	48			surf = .025
	30	77			surf = .025
	20	50			surf = .05
	30	90			surf = .05
Li and Chen, 2002	0.5	50			partitioning
	5	75			partitioning
	10	100			partitioning
	0.5	5			reduced radius
	5	10			reduced radius
	10	17			reduced radius
Ghannam and Chaalal, 2003	10	5			still water
	20	150			still water
	30	260			still water
	10	5			circulated water
	20	16			circulated water
	30	36			circulated water
Sayyouh et al., 1993	5			20	
	10			90	
	15			3	
	20			60	
Guyomarch et al., 2002	10	0			
	25	166			
	35	200			
	50	566			

23

Table 16 Results of Metabolite Uptake (from Wolfe et al., 1998)

| Sample | Metabolic Uptake (as percentage recovered) | | | |
| | A,b Napthol Sulphate | | Napthalene | |
	22 o/oo	34 o/oo	22 o/oo	34 o/oo
20 C WAF - Control	1	2	98	96
20 C WAF - Exp. Med.	5	8	93	90
20 C WAF - Algae	4	1	80	85
20 C Disp. oil - Control		2	99	96
20 C Disp. oil - Exp. Med.	3	3	96	95
20 C Disp. oil - Algae			95	92
12 C WAF - Control	6	1	91	98
12 C WAF - Exp. Med.	6	3	91	96
12 C WAF - Algae			92	92
12 C Disp. oil - Control	4		94	99
12 C Disp. oil - Exp. Med.	5	3	93	96
12 C Disp. oil - Algae			90	95

| Table 17	Recent Salinity Measurement Results						
Summer Sampling Data - June 24, 2004							
Location	Bligh Reef	Outer Jack Bay	Shoup Bay	Gold Creek	Mineral Creek	Glacial Creek	Lowe River
Latitude	60 47.926	61 02.305	61 07.612	61 07.533	61 07.53	61 06.183	61 05.778
Longitude	146 51.617	146 38.819	146 35.263	146 29.137	146 25.580	146 17.464	146 17.794
Surface Salinity o/oo	26.3	15.3	4.3	2.7	1.2	0.2	0.4
Temperature oC	13.6	15.6	7.2	10.3	10.6	3.6	5.3
Fall Sampling September 24, 2004							
Location		Outer Jack Bay		Gold Creek			Lowe River
Latitude		61 02.210		61 07.710			61 05.779
Longitude		146 40.191		146 28.828			146 17.723
Surface Salinity o/oo		20.6		17.7			2.7
Temperature oC		9.1		8.3			5.9

24
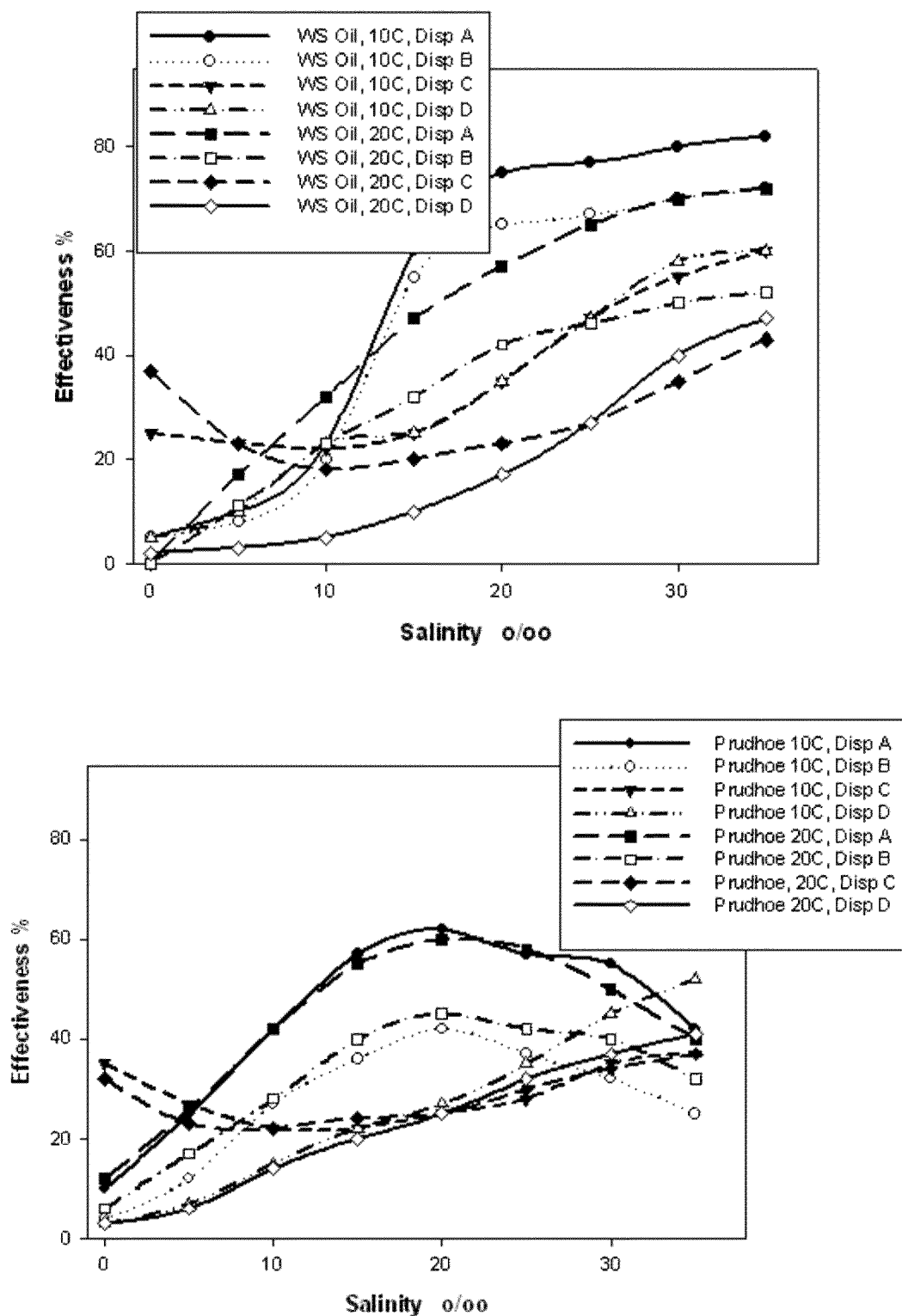
Figure 1   Salinity and Dispersant Test Results from Belk et al., 1989, Warren Springs Oil, Upper
Plot: Prudhoe Bay Oil Lower Plot
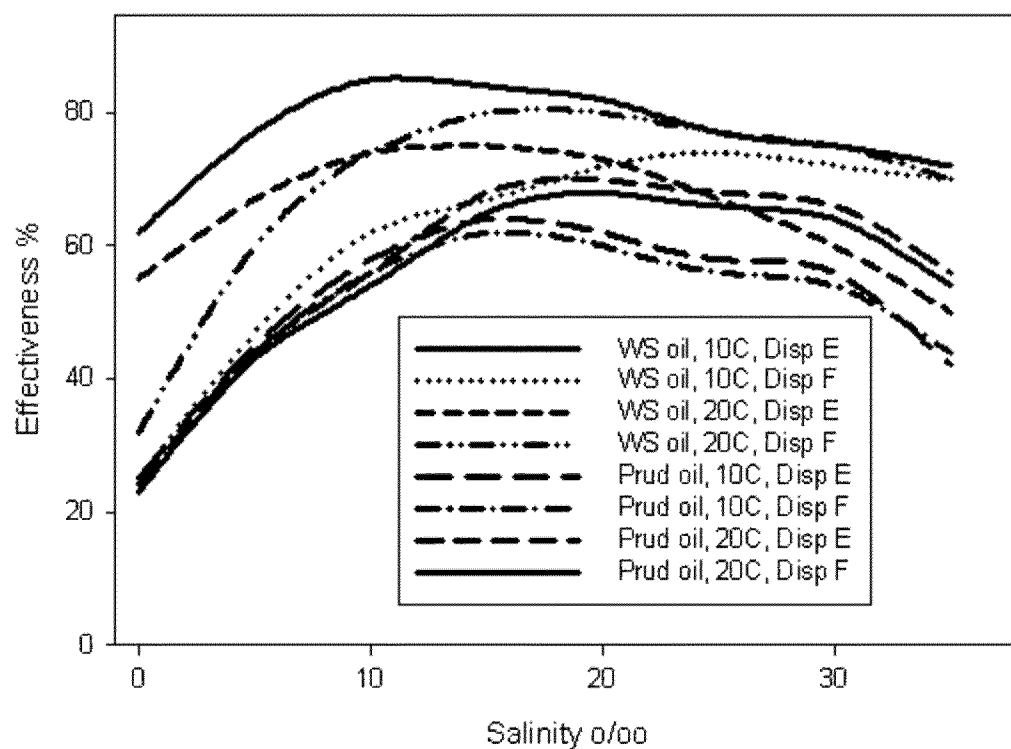
25

Figure 2   Dispersant E and F Data from Belk et al., 1989
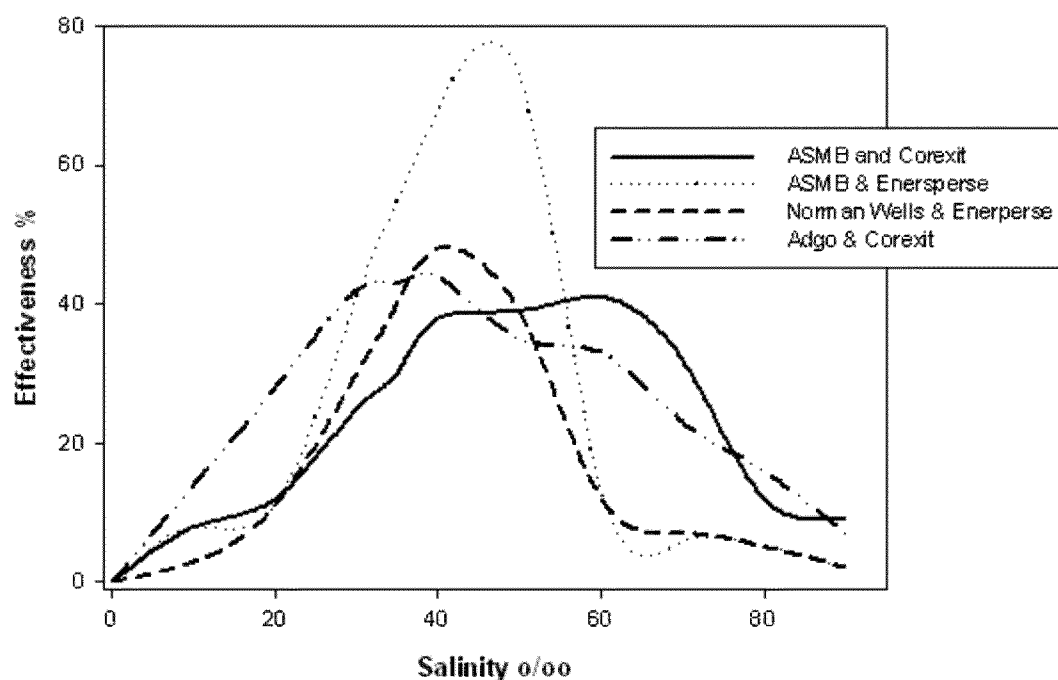

Figure 3   Dispersant Effectiveness with Salinity from Fingas et al. 1991
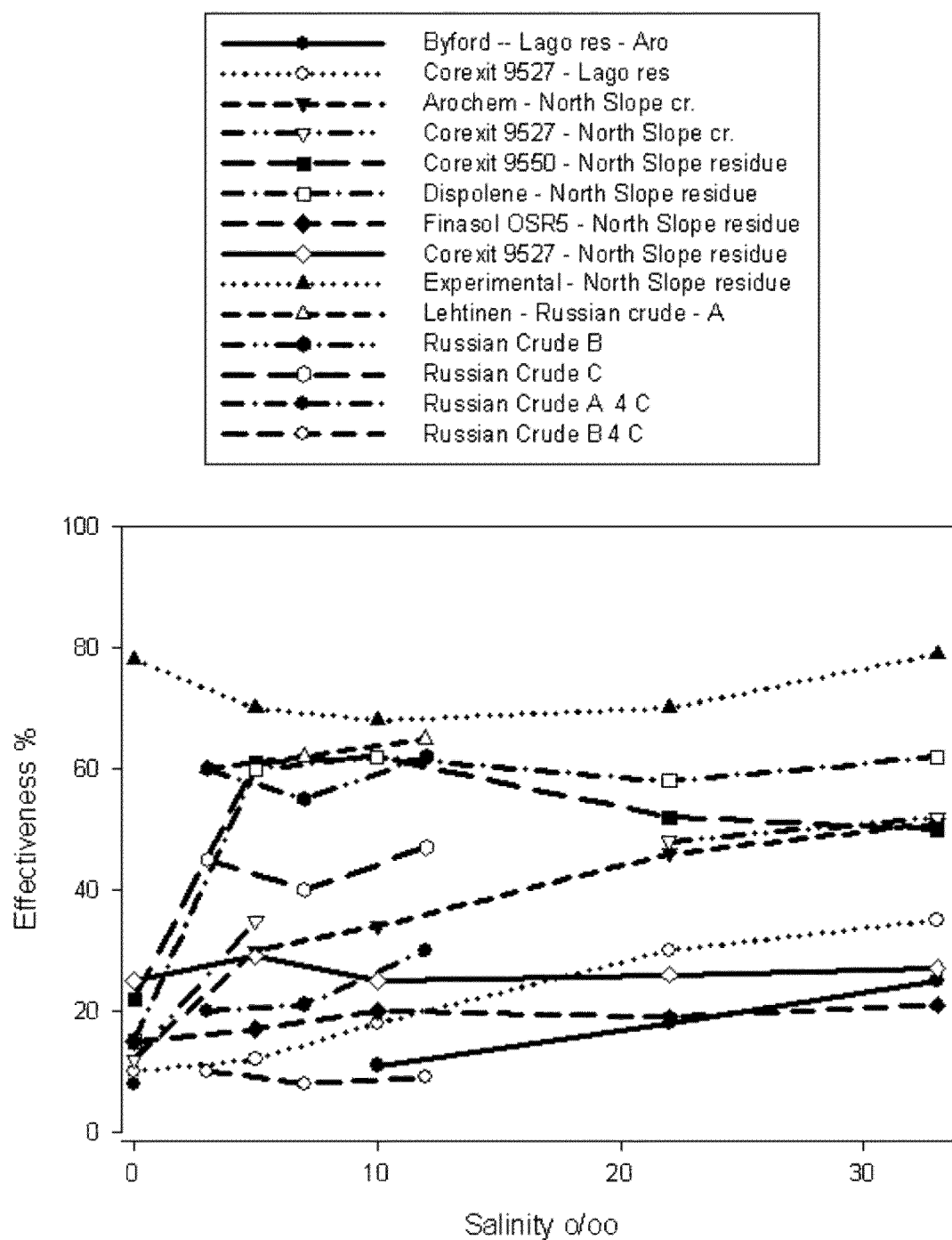
26

Figure 4   Salinity and Dispersant Effectiveness Data from Byford et al., 1983 and Lehtinen and Vesala, 1984
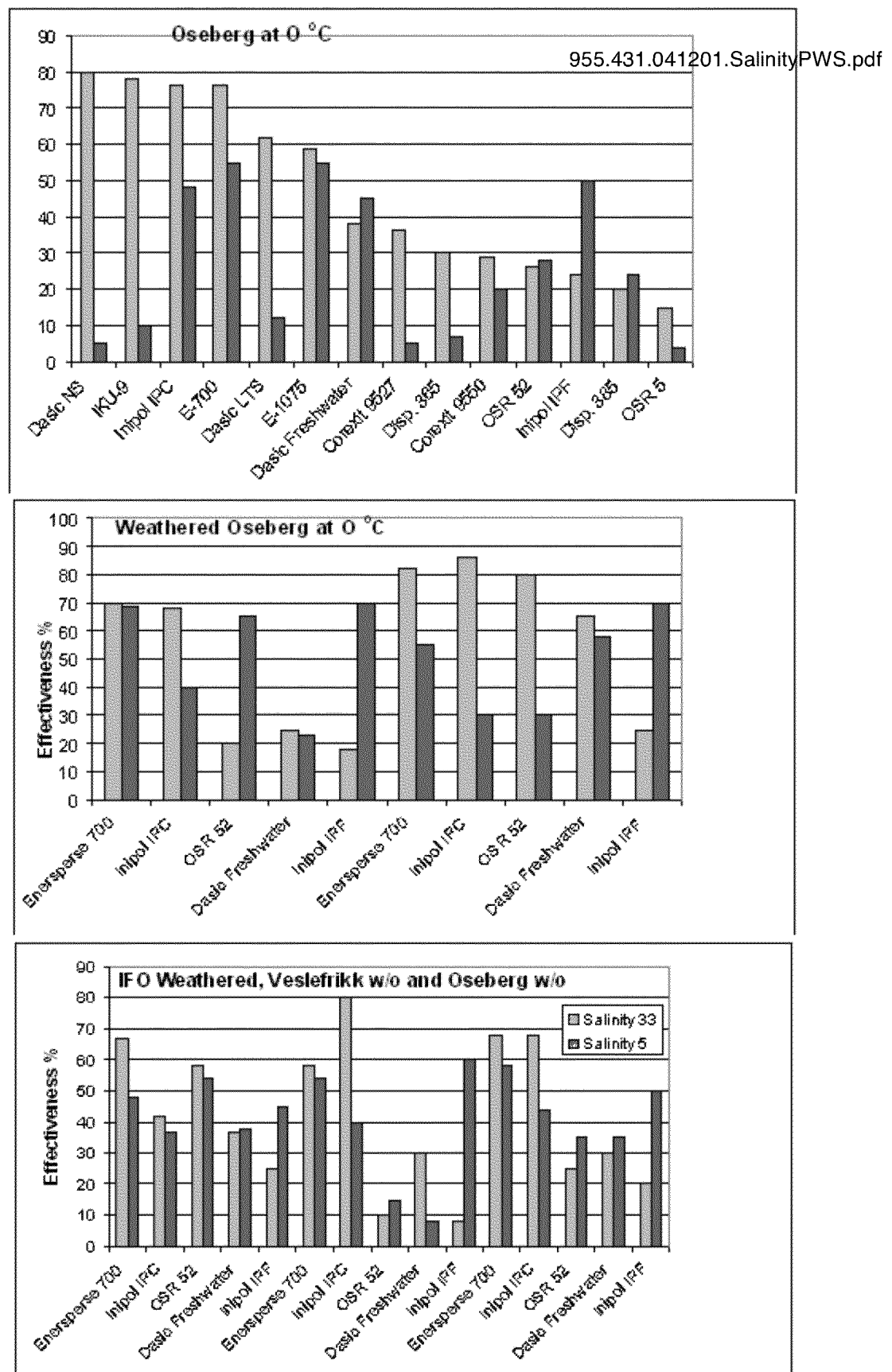
27

Figure 5   Dispersant Effectiveness with Salinity from Brandvik et al. 1995
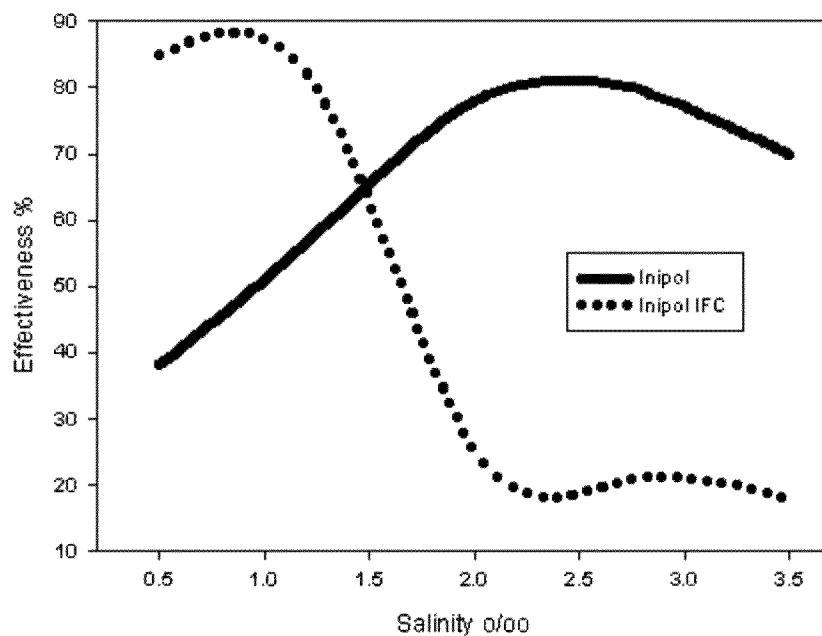
28

Figure 6   Dispersant/Salinity Test on Two Inipol dispersants - Inipol IFC was a Special
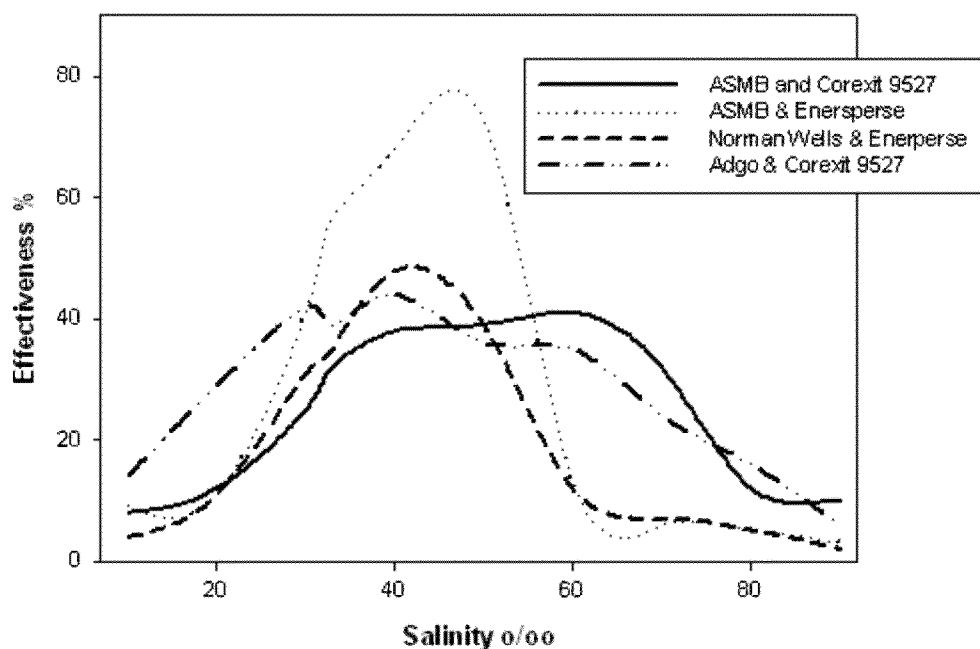Freshwater Dispersant (Data from Brandvik and Daling, 1992)

Figure 7   Tests on Dispersant Effects with Varying Salinity (Data from Fingas et al., 1994)
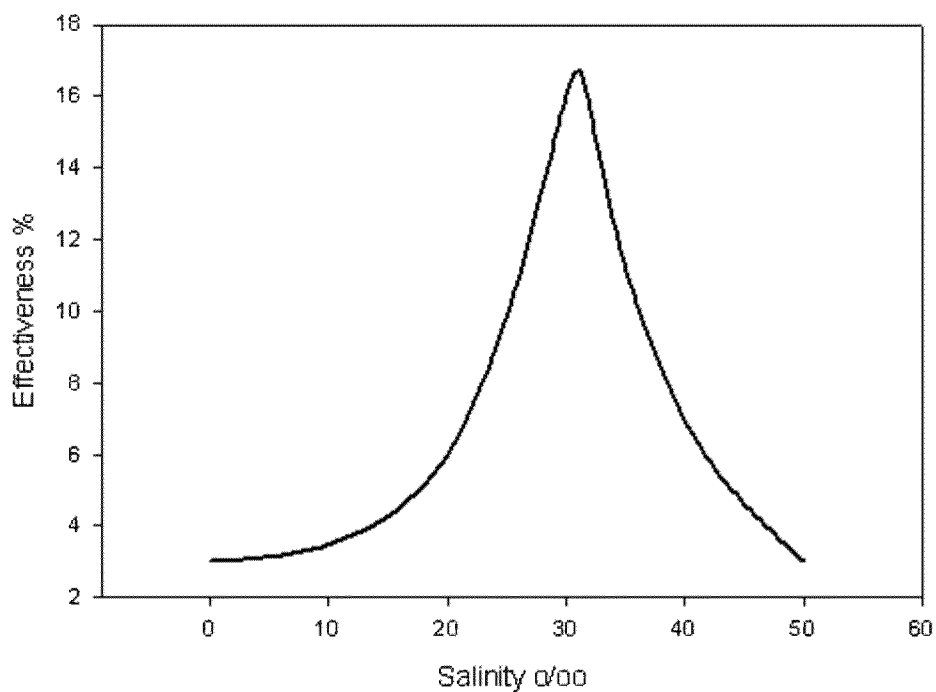
29

Figure 8   Dispersant Effectiveness Data for Corexit 9527 and a Light Arabian Crude (Data from Moet et al., 1995)
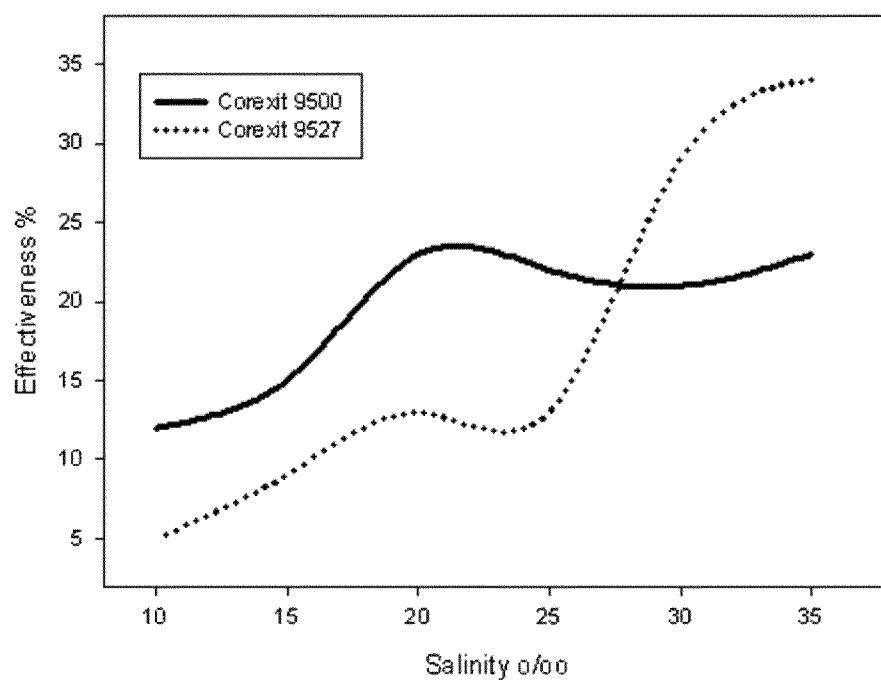

Figure 9   Dispersant Effectiveness Data on ANS Crude (Data from Blondina et al., 1997 a,b)
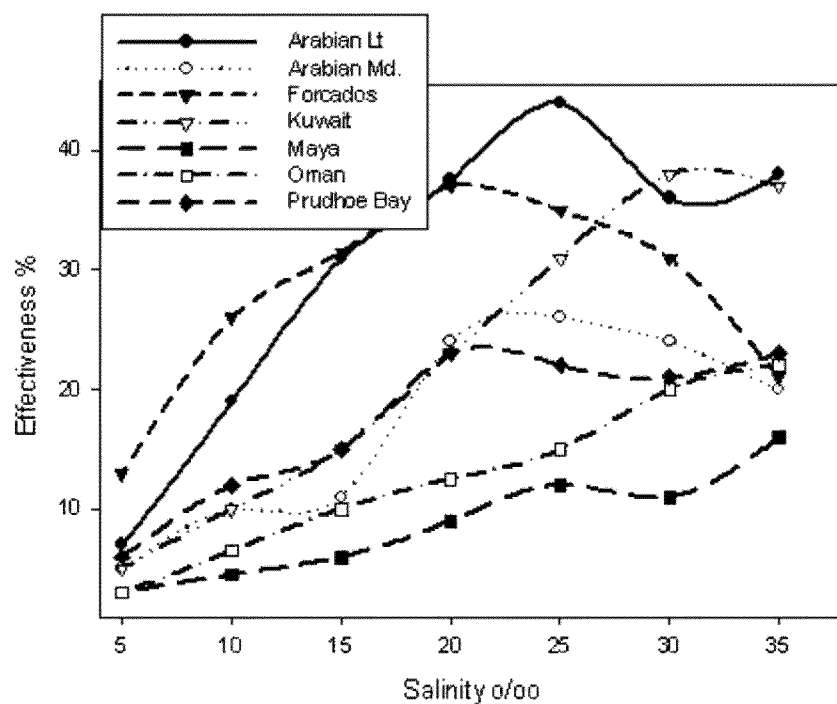
30

Figure 10   Effectiveness of Corexit 9500 with Salinity (Data from Blondina et al., 1999)
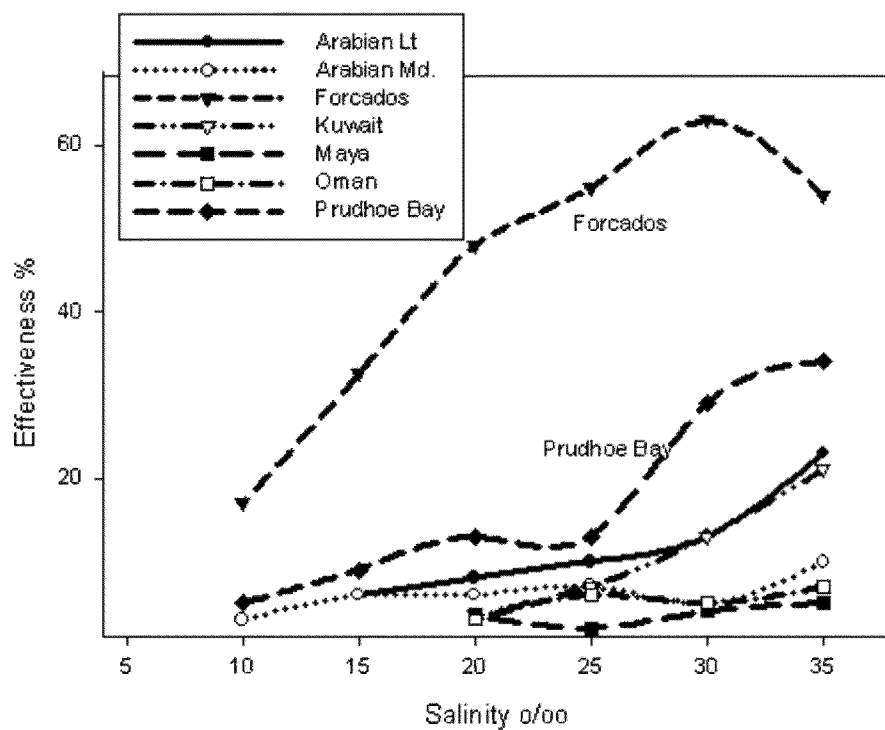

Figure 11   Effectiveness of Corexit 9527 with Salinity (Data from Blondina et al., 1999)

31

Figure 12   Three-way Relationship of Effectiveness, Salinity, and Temperature for Corexit 9527 and Fresh ANS (Data from Moles et al., 2002)
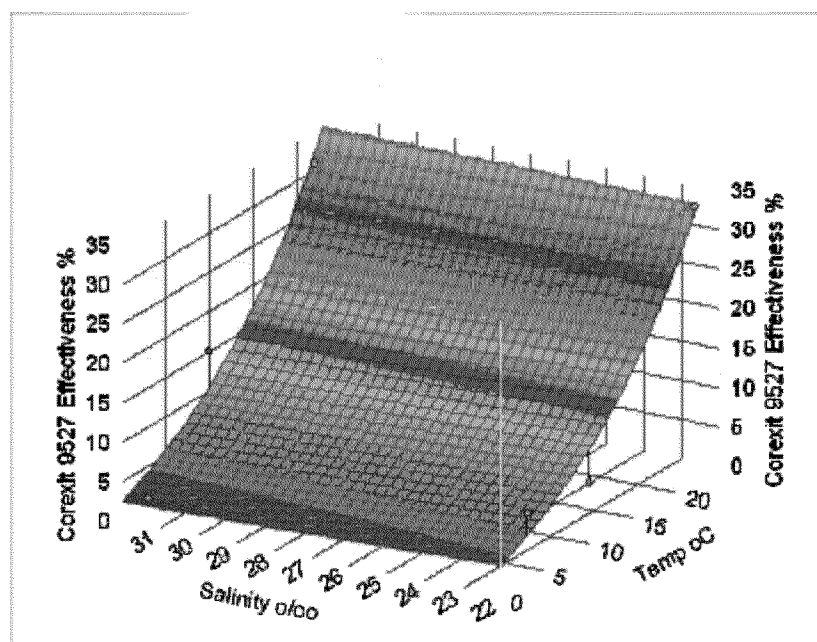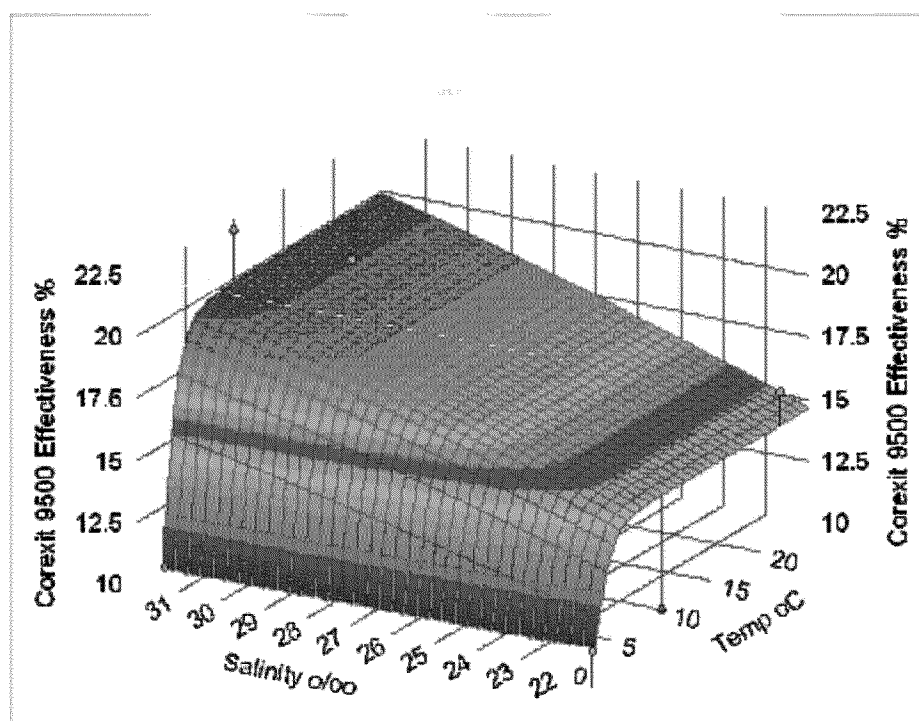

Figure 13   Three-way Relationship of Effectiveness, Salinity and Temperature for Corexit 9500 and Fresh ANS (Data from Moles et al., 2002)
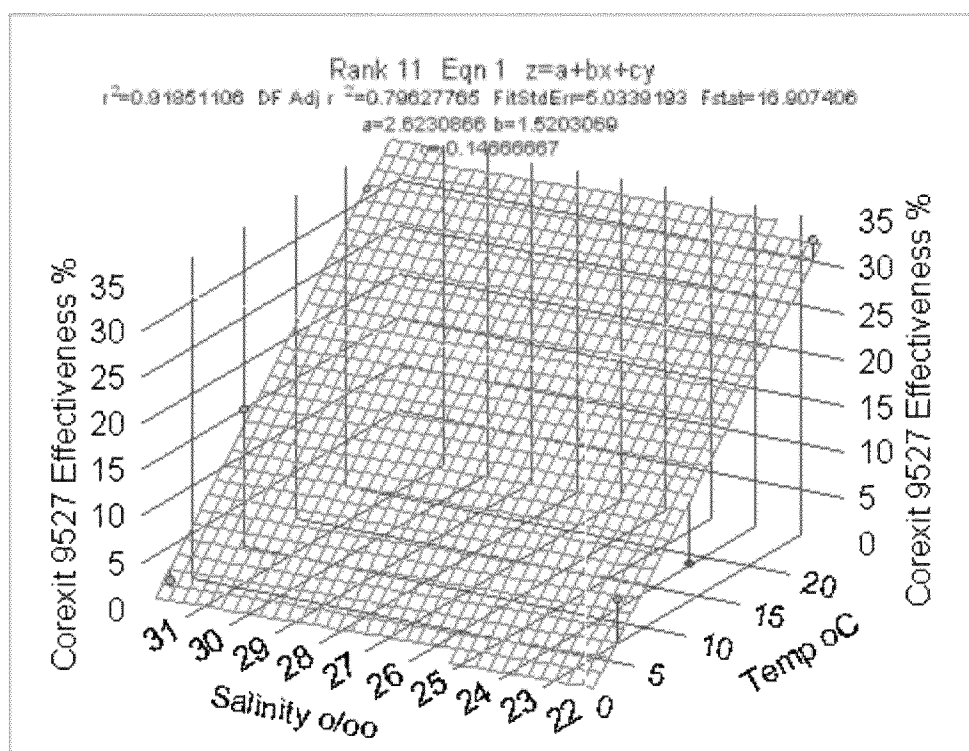
32

Figure 14   Three-Way Correlation of Corexit 9527 Effectiveness with Fresh ANS (Moles et al., 2002)
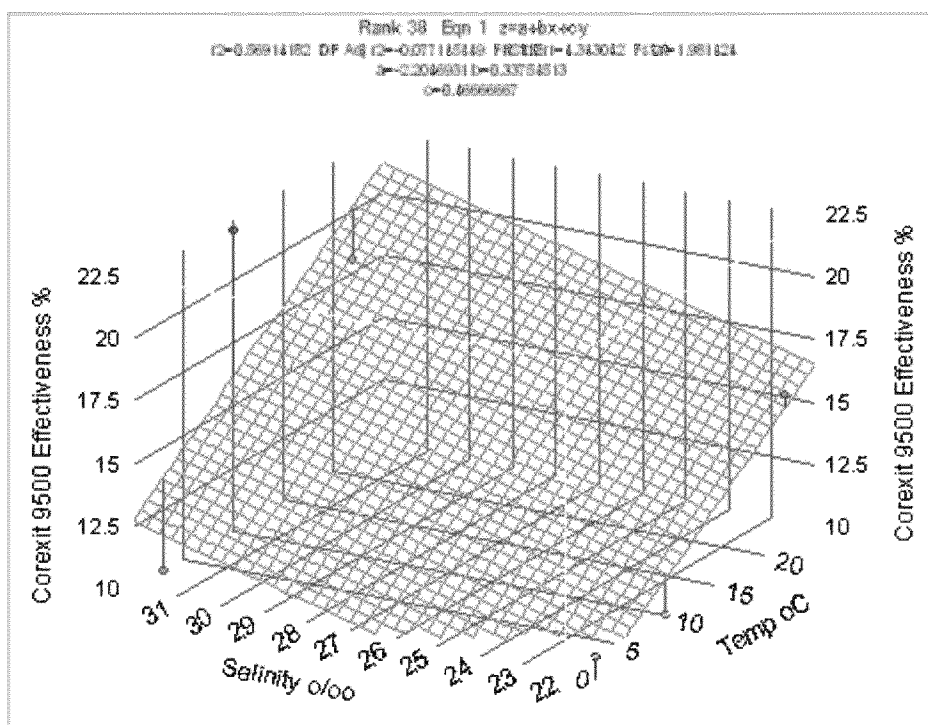
Figure 15   Three-Way Correlation of Corexit 9500 Effectiveness with Fresh ANS (Moles et al., 2002)

33
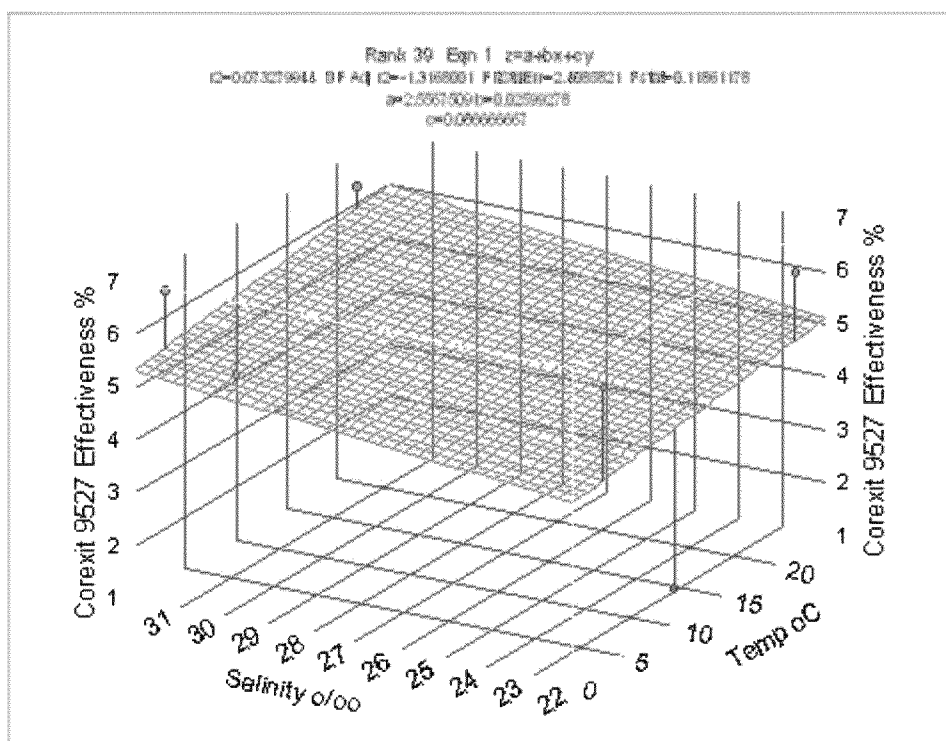
Figure 16   Three-Way Correlation of Corexit 9527 Effectiveness with Weathered ANS (Data from Moles et al., 2002)
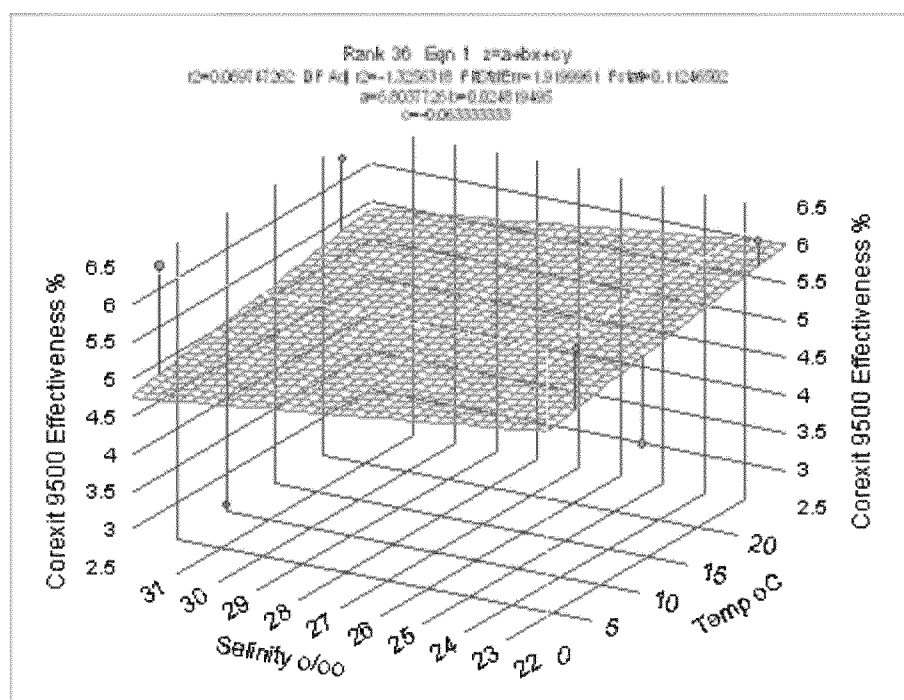
Figure 17   Three-Way Correlation of Corexit 9500 Effectiveness with Weathered ANS (Data from Moles et al., 2002)

34
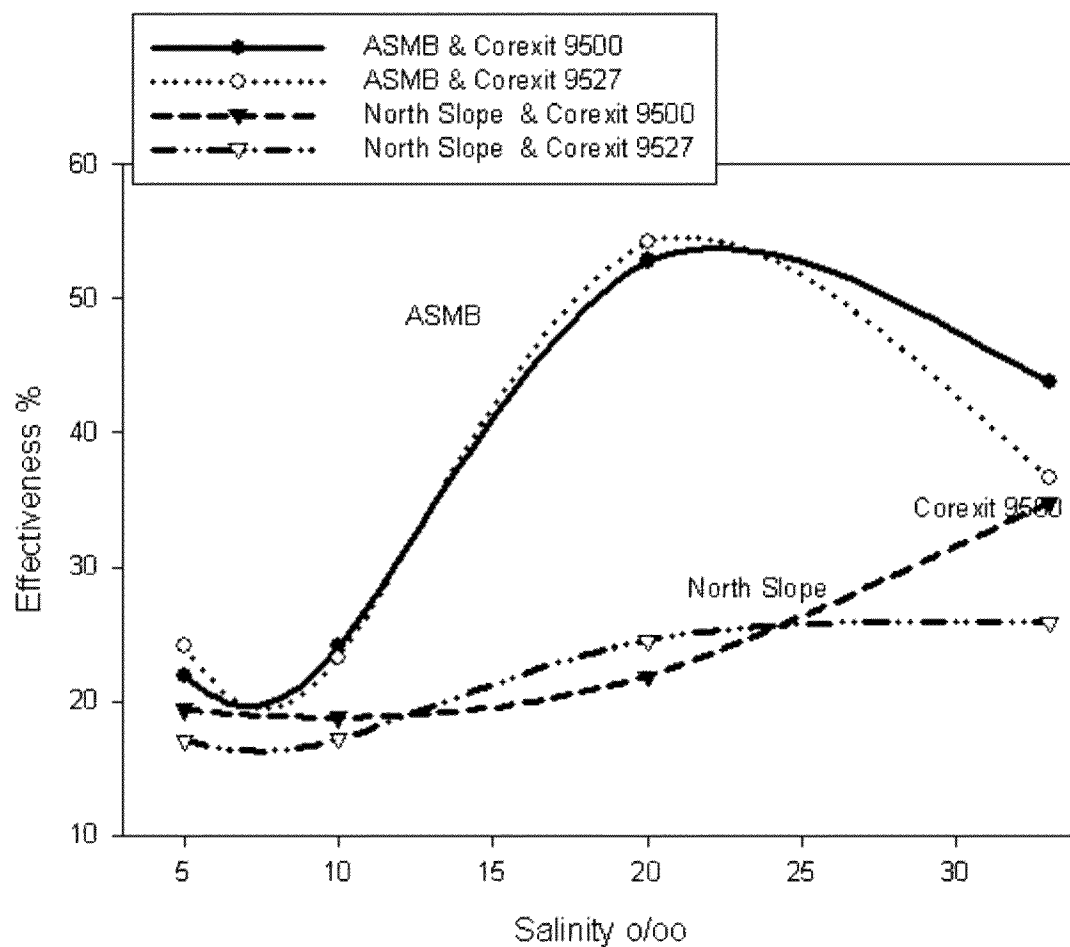
Figure 18   Variation of Dispersant Effectiveness with Salinity (Data from Fingas et al., 2003)

35
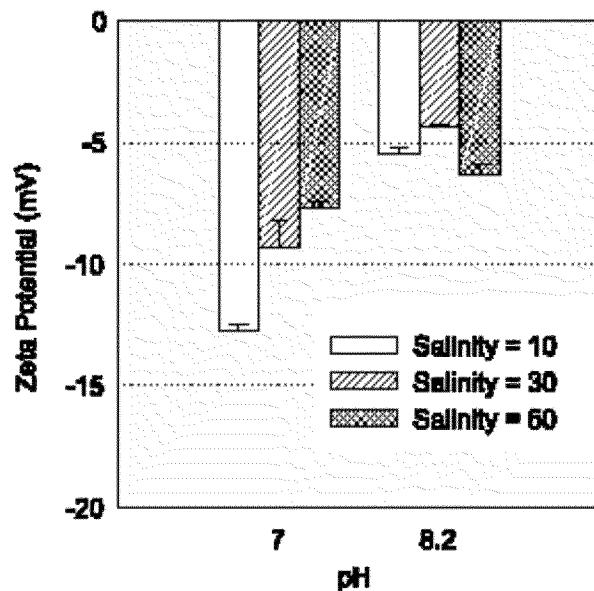
Figure 19 Measured Zeta Potential Values of Chemically Dispersed Crude Oil Droplets at
Selected pH Values (Data from Sterling et al., 2004)
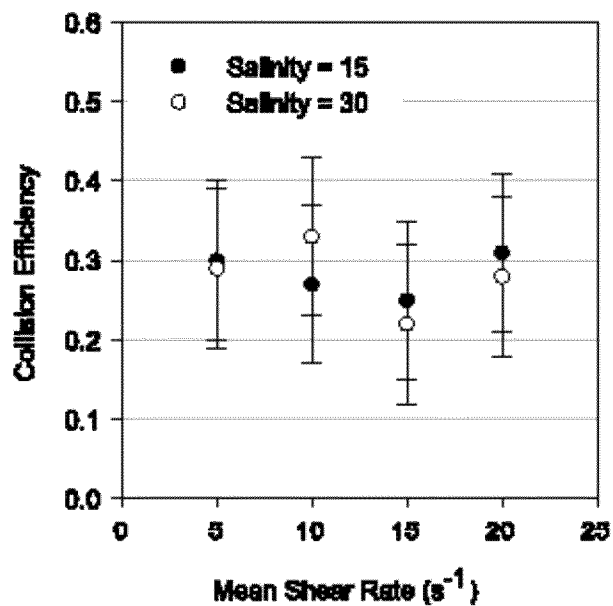
Figure 20   Effect of Shear Rate on Collision Efficiency (Data from Sterling et al., 2004)

36
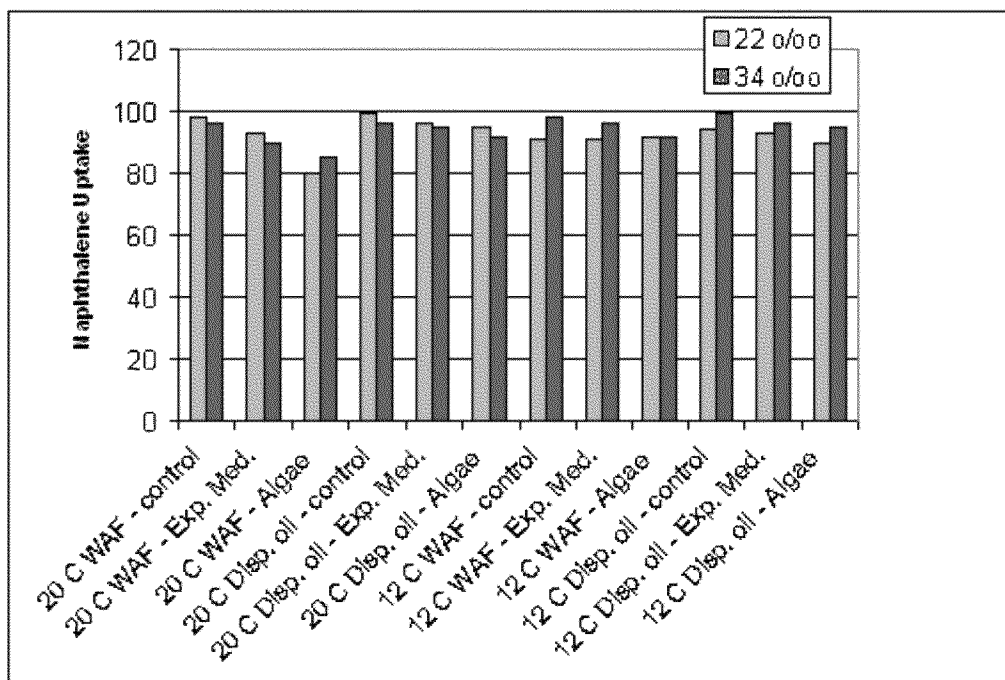
Figure 21   Variation in Uptake of Naphthalene by Algae (Data from Wolfe et al., 1998)
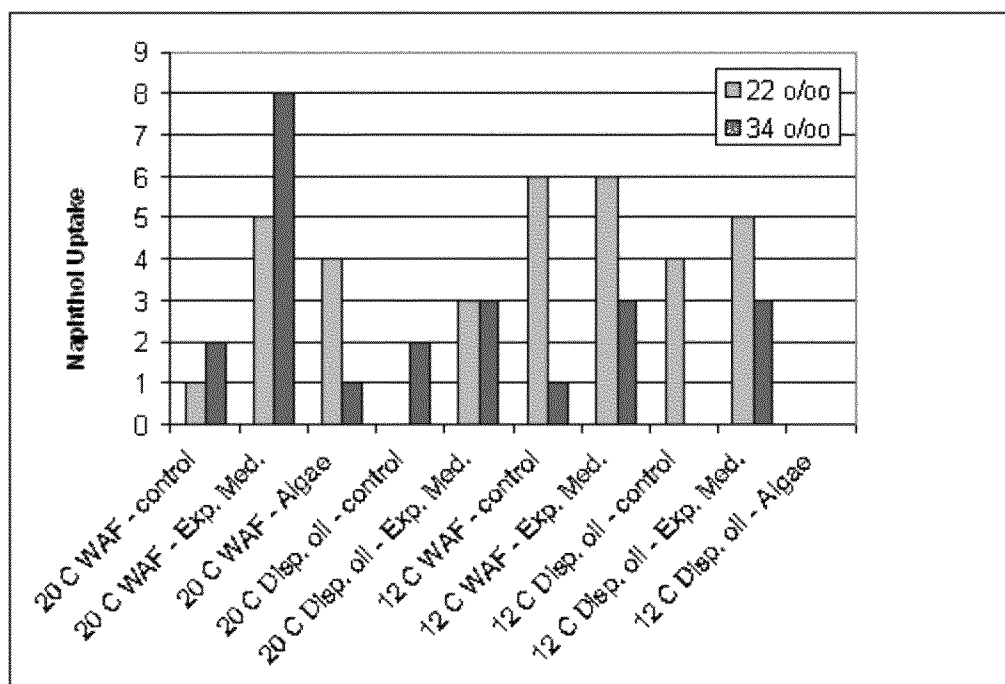
Figure 22   Variation in Uptake of a,b Naphthol Sulphate by Algae (Data from Wolfe et al., 1998)

37
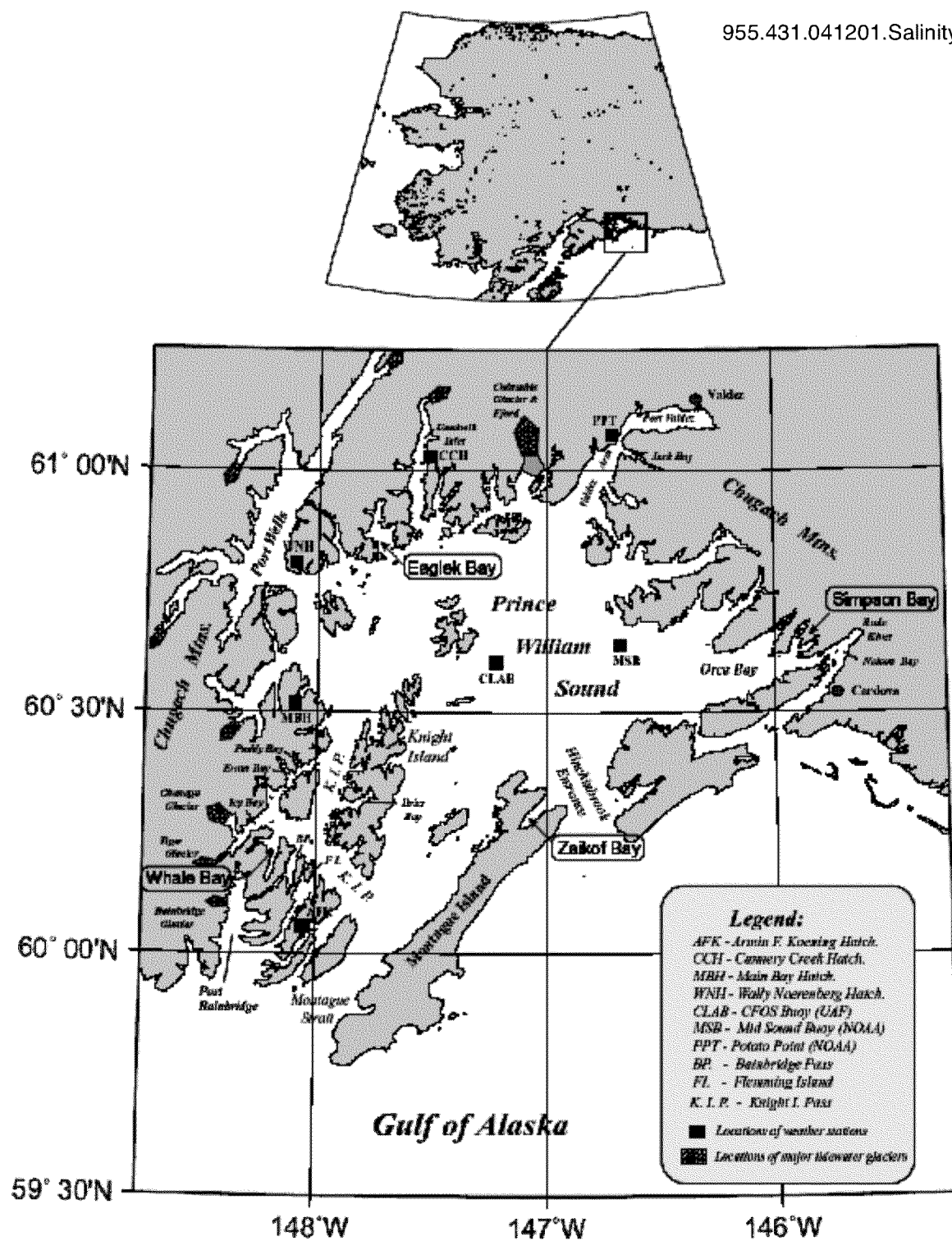
Figure 23 An Overview of Prince William Sound Showing Detailed Sample Sites
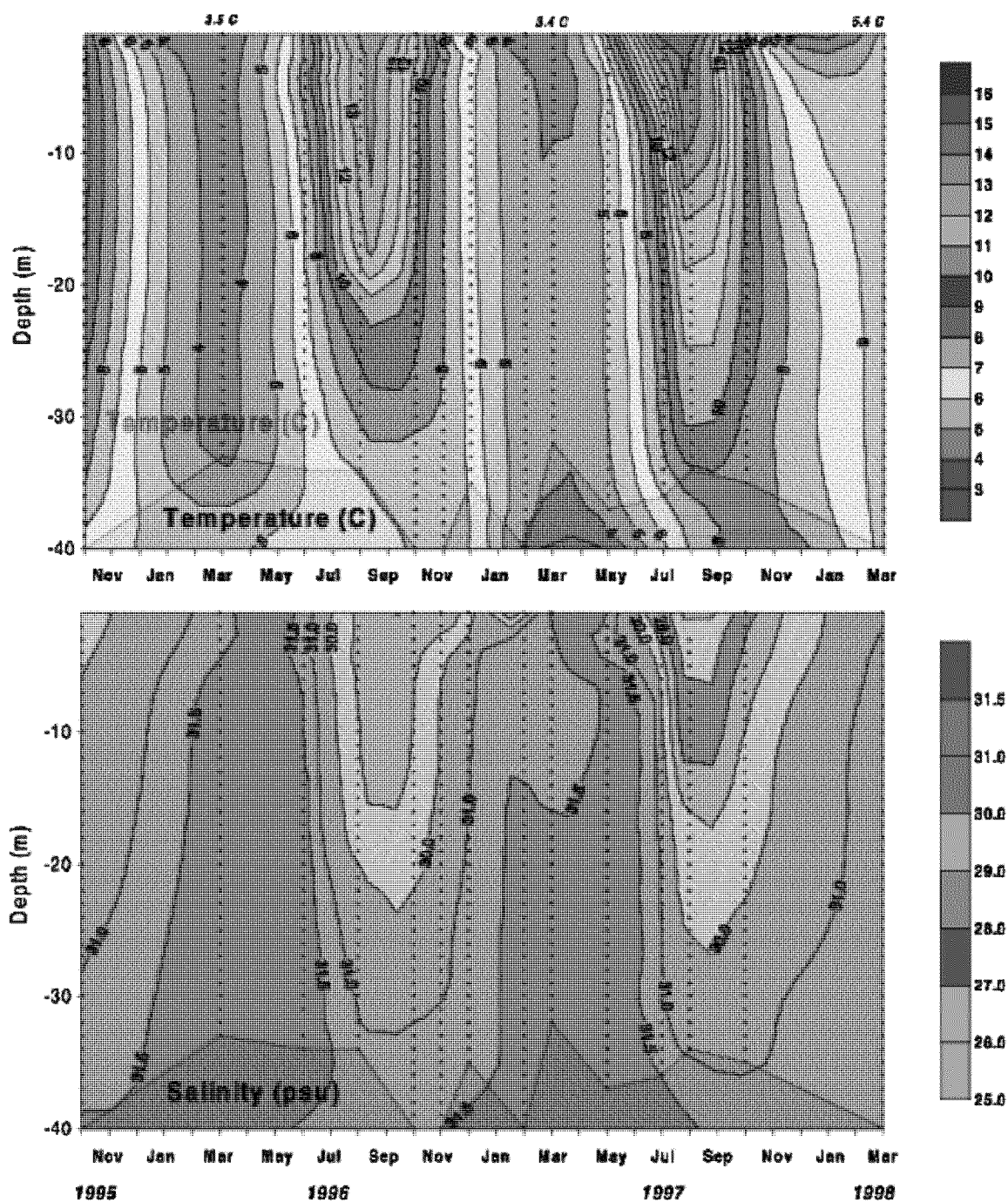
Figure 24 A Temperature/Salinity Graph from Zaikof Bay Sampling Site (Vaughn et al., 2001)

Eaglek Bay, Station 16
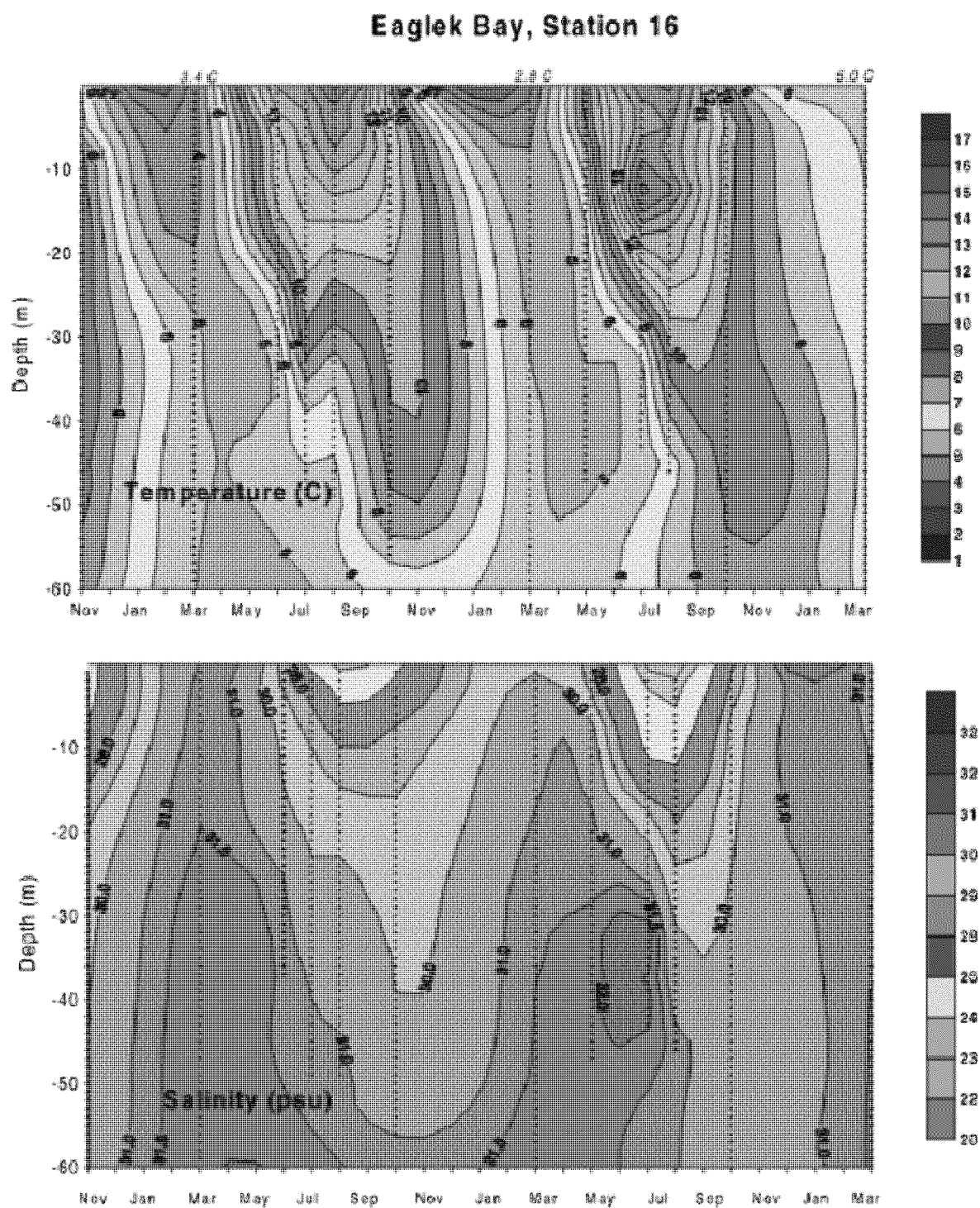
Figure 25   A Temperature/Salinity Graph from Eaglek Bay Sampling Site (Vaughn et al., 2001)

40
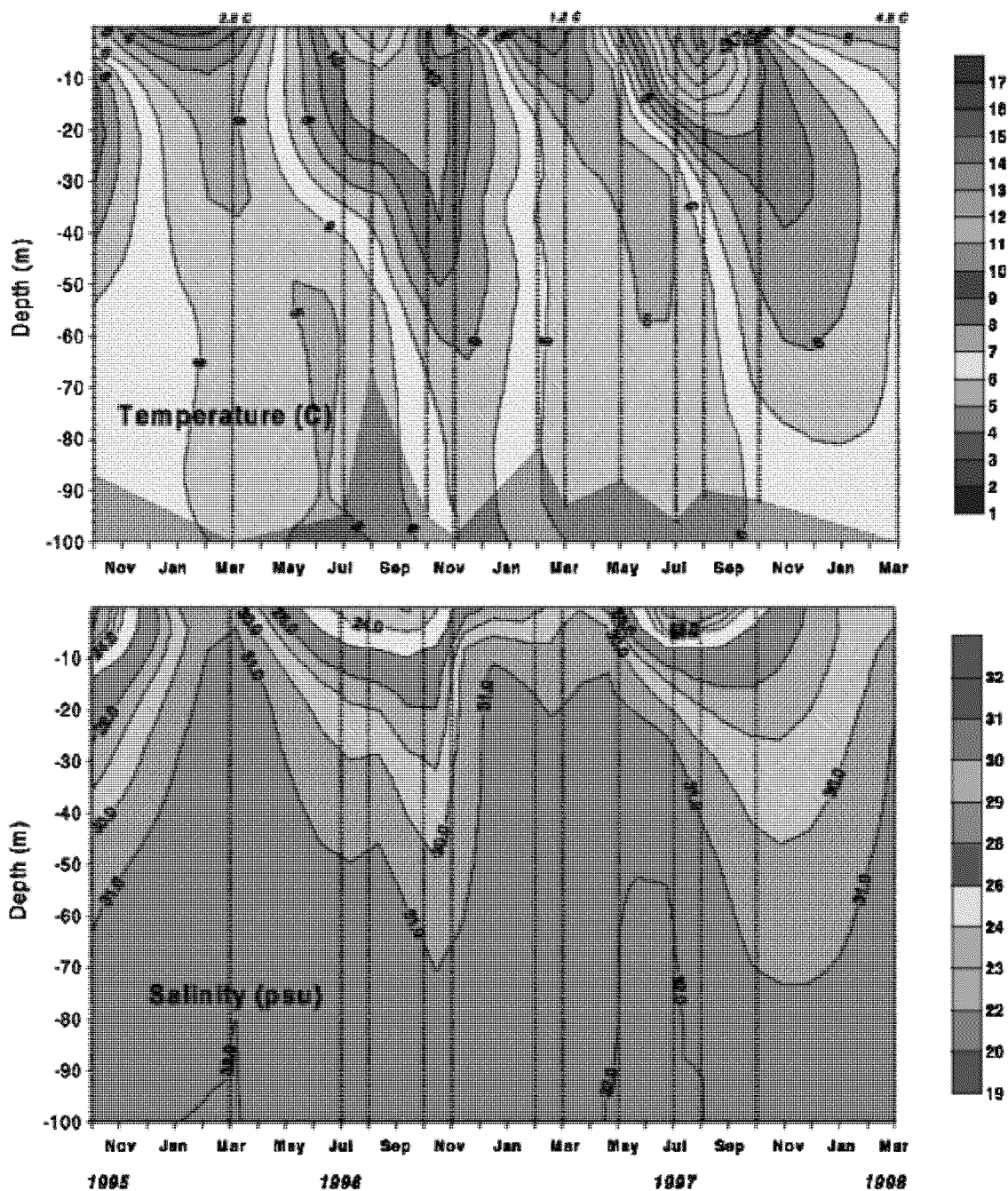
Figure 26 A Temperature/Salinity Graph from Whale Bay Sampling Site (Vaughn et al., 2001)
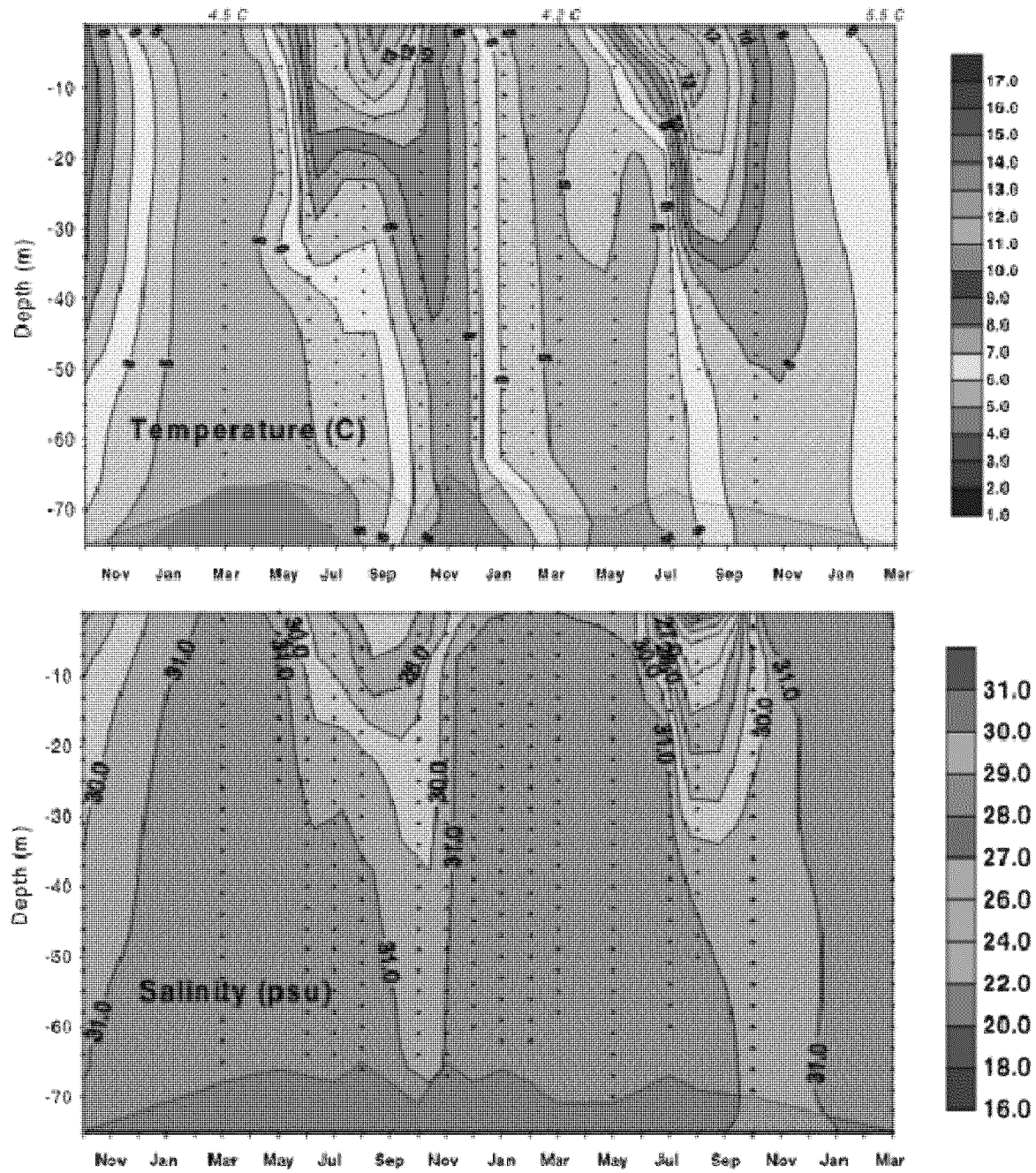
Figure 27 A Temperature/Salinity Graph from Simpson Bay Sampling Site (Vaughn et al., 2001)

10. References

Abuin, E.B., M.A. Rubio and E.A. Lissi, "Solubility of Water in Water-in-Oil Microemulsions Stabilized by Cetyltrimethylammonium: Effects of the Surfactant Counterion, the Nature and Composition of the Oil and the Salinity of the Droplets", *Journal of Colloid and Interface Science*, 158, pp. 129-132, 1993.

Al-Roomi, Y., R. George, A. Egibaly and A. Elkamel, "Use of a Novel Surfactant for Improving the Transportability/transportation of Heavy/viscous Crude Oils", *Journal of Petroleum Science and Engineering*, 42, pp. 234-243, 2004.

Austad, T. and S. Strand, "Chemical Flooding of Oil Reservoirs 4. Effects of Temperature and Pressure on the Middle Phase Solubilization Parameters Close to Optimum Flood Conditions", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 108, pp. 243-252, 1996.

Austad, T., I. Fjelde, K. Veggeland and K. Taugbøl, "Physicochemical Principles of Low Tension Polymer Flood", *Journal of Petroleum Science and Engineering*, 10, pp. 255-269, 1994.

Babadagli, T., "Selection of Proper Enhanced Oil Recovery Fluid for Efficient Matrix Recovery in Fractured Oil Reservoirs", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 223, pp. 157-173, 2003.

Bang, I. and C.N.K. Mooers, "The Influence of Several Factors Controlling the Interactions between Prince William Sound, Alaska and the Northern Gulf of Alaska", *Journal of Physical Oceanography*, 33, pp. 19-36, 2003.

Becher, P., *Emulsions: Theory and Practice*, Robert E. Krieger Publishing Company, Huntington, NY, 1977.

Belk, J.L., D.J. Elliott and L.M. Flaherty, "The Comparative Effectiveness of Dispersants in Fresh and Low Salinity Waters", in *Proceedings of the 1989 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp. 333-336, 1989.

Blondina, G.J., M.L. Sowby, M.A. Ouano, M.M. Singer and R.S. Tjeerdema, "Comparative Efficacy of Two Corexit Dispersants as Measured Using California's Modified Swirling Flask Test", in *Proceedings of the Twentieth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, ON, pp. 561-573, 1997a.

Blondina, G.J., M.L. Sowby, M.T. Ouano, M.M. Singer and R.S. Tjeerdema, "A Modified Swirling Flask Efficacy Test for Oil Spill Dispersants", *Spill Science and Technology Bulletin*, 4, pp. 177-185, 1997b.

Blondina, G.J., M.M. Singer, I. Lee, M.T. Ouano, M. Hodgins, R.S. Tjeerdema and M.L. Sowby, "Influence of Salinity on Petroleum Accommodation by Dispersants", *Spill Science & Technology Bulletin*, 5(2), pp. 127-134, 1999.

Brandvik, P.J. and P.S. Daling, "Laboratory Testing of Dispersants Under Arctic Conditions", in *Proceedings of the Fifteenth Arctic Marine Oilspill Program Technical Seminar*, Environment

Canada, Ottawa, ON, pp. 123-134, 1992.

Brandvik, P.J., O.O. Knudsen, M.O. Moldestad and P.S. Daling, "Laboratory Testing of Dispersants Under Arctic Conditions", in *The Use of Chemicals in Oil Spill Response,* STP 1252, American Society for Testing and Materials, Philadelphia, PA, pp. 191-206, 1995.

Brown, H.M. and R.H. Goodman, "Dispersants in the Freshwater Environment", in *Oil Dispersants: New Ecological Approaches*, STP 1018, American Society for Testing and Materials, Philadelphia, PA, pp. 31-40, 1989.

Brown, H.M., J.S. Goudey, J.M. Foght, S.K. Cheng, M. Dale, J. Hoddinott, L.R. Quaife and D.W.S. Westlake, "Dispersion of Spilled Oil in Freshwater Systems: Field Trial of a Chemical Dispersant", *Oil and Chemical Pollution*, 6, pp. 37-54, 1990.

Byford, D.C., P.J. Green and A. Lewis, "Factors Influencing the Performance and Selection of Low-Temperature Dispersants", in *Proceedings of the Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, ON, pp. 140-150, 1983.

Chen, H., L. Han, P. Luo and Y. Ye, "The Interfacial Tension between Oil and Gemini Surfactant Solution", *Surface Science*, 552, pp. L53-L57, 2004.

Chooro, M., N. Kamenka, B. Faucompre, S. Partyka, M. Lindheimer and R. Zana, "Miscellization and Adsorption of a Zwitterionic Surfactant: N-dodecyl Betaine - Effect of Salt", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 110, pp. 249-261, 1996.

Clayton, J.R., G.H. Farmer, J.R. Payne, G.D. McNabb, P.C. Harkins, J.S. Evans, N.P. Rottlunda, C.R. Phillips and M.L. Evans, "Effects of Chemical Dispersant Agents on the Behavior and Retention of Spilled Crude Oil in a Simulated Streambed Channel", in *Oil Dispersants: New Ecological Approaches*, STP 1018, L.M. Flaherty (ed.), American Society for Testing and Materials, Philadelphia, PA, pp. 4-24, 1989.

Clayton, J.R., Jr., J.R. Payne, S.-F. Tsang, V. Frank, P. Marsden and J. Harrington, "Chemical Oil Spill Dispersants: Update State-of-the-Art on Mechanism of Action and Laboratory Testing for Performance", EPA/600/S-92/065, United States Environmental Protection Agency, Cincinnati, OH, 6 p., 1992.

Clayton, Jr., J.R., J.R. Payne and J.S. Farlow, *Oil Dispersants: Mechanisms of Action and Laboratory Tests*, C.K. Smoley for CRC Press, Boca Raton, FL, 103 p., 1993.

Davis, H.T., "Factors Determining Emulsion Type: Hydrophile-lipophile Balance and Beyond", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 91, pp. 9-241, 1994.

Drummond, C. and J. Israelachvili, "Surface Forces and Wettability", *Journal of Petroleum Science and Engineering*, 33(1-3), pp. 123-133, 2002.

Fingas, M.F., I. Bier, M. Bobra and S. Callaghan, "Studies on the Physical and Chemical Behaviour of Oil and Dispersant Mixtures", in *Proceedings of the 1991 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp. 419-426, 1991.

44

Fingas, M.F., D.A. Kyle and E.J. Tennyson, "Physical and Chemical Studies on Oil Spill Dispersants: Effectiveness Variation with Energy", in *Proceedings of the Fifteenth Arctic and Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, ON, pp. 135-142, 1992.

Fingas, M.F., D.A. Kyle, Z. Wang, F. Ackerman and J. Mullin, "Testing of Oil Spill Dispersant Effectiveness in the Laboratory", in *Proceedings of the Seventeenth Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, ON, pp. 905-941, 1994.

Fingas, M.F., D.A. Kyle, P. Lambert, Z. Wang and J.V. Mullin, "Analytical Procedures for Measuring Oil Spill Dispersant Effectiveness in the Laboratory", in *Proceedings of the Eighteenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, ON, pp. 339-354, 1995a.

Fingas, M.F., D.A. Kyle and E.J. Tennyson, "Dispersant Effectiveness: Studies Into the Causes of Effectiveness Variations", in *The Use of Chemicals in Oil Spill Response*, STP 1252, American Society for Testing and Materials, Philadelphia, PA, pp. 92-132, 1995b.

Fingas, M.F., Z. Wang, B. Fieldhouse and P. Smith, "Dispersed Oil Resurfacing with Time", in *Proceedings of the Twenty-Sixth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, ON, pp. 731-742, 2003.

Fjelde, I. and T. Austad, "HPLC Analysis of Salt Tolerant Mixtures of Ethoxylated and Non-ethoxylated Sulfonates Applicable in Enhanced Oil Recovery", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 82, pp. 85-90, 1994.

Fjelde, I., T. Austad and J. Miller, "Adsorption VII. Dynamic Adsorption of a Dual Surfactant System onto Reservoir Cores at Seawater Salinities", *Journal of Petroleum Science and Engineering*, 13, pp. 193-201, 1995.

Flaherty, L.M., W.B. Katz and S. Kaufman, "Dispersant Use Guidelines for Freshwater and Other Inland Environments", in *Oil Dispersants: New Ecological Approaches*, STP 1018, L.M. Flaherty (ed.), American Society for Testing and Materials, Philadelphia, PA, pp. 25-30, 1989.

Fritz, D.E., "Effect of Salinity on Chemical Effectiveness", in *Proceedings of a Workshop on the Use of Chemical Countermeasures Product Data for Oil Spill Planning and Response*, NOAA, Seattle, WA, pp. 75-81, 1995.

Gay, S.M. and S.L. Vaughn, "Seasonal Hydrography and Tidal Currents of Bays and Fjords in Prince William Sound, Alaska", *Fisheries Oceanography*, 10(Suppl. 1), pp. 159-193, 2001.

George-Ares, A., R.R. Lessard, K.W. Becker, G.P. Canevari and R.J. Fiocco, "Modification of the Dispersant Corexit 9500 for Use in Freshwater", in *Proceedings of the 2001 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp. 1209-1211, 2001.
Ghannam, M.T. and O. Chaalal, "Oil Spill Cleanup Using Vacuum Technique", *Fuel*, 82, pp. 789-797, 2003.

45

Guyomarch, J., S. Le Floch and F.-X. Merlin, "Effect of Suspended Mineral Load, Water Salinity and Oil Type on the Size of Oil-Mineral Aggregates in the Presence of Chemical Dispersant", *Spill Science and Technology*, 8, pp. 95-100, 2002.

Hou, W. and K.D. Papadopoulis, "$W_1/O/W_2$ and $O_1/W/O_2$ Globules Stabilized with Span 80 and Tween 80", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, Vol. 125, pp. 181-187, 1997.

Hou, W. and K.D. Papadopoulis, "Stability of Water-in-oil-in-water Type Globules", *Chemical Engineering Science*, 51, pp. 5043-5051, 1996.

Kaczmarski, J.P., M-R. Tarng, Z. Ma and J.E. Glass, "Surfactant and Salinity Influences on Associative Thickener Aqueous Solution Rheology", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 147, pp. 39-53, 1999.

Kjøniksen, A-L., B. Nyström and B. Lindman, "Dynamic Light Scattering on Semidilute Aqueous Systems of Ethyl (hydroxyethyl) Cellulose. Effects of Temperature, Surfactant Concentration, and Salinity", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 149, pp. 347-354, 1999.

Lehtinen, C.M. and A.M. Vesala, "Effectiveness of Oil Spill Dispersants at Low Salinities and Low Water Temperatures", in *Oil Spill Chemical Dispersants: Research, Experience and Recommendations*, T.E. Allen (ed.), STP 840, American Society for Testing and Materials, Philadelphia, PA, pp. 108-121, 1984.

Li, J.-L. and B.-H. Chen, "Solubilization of Model Polycyclic Aromatic Hydrocarbons by Nonionic Surfactants", *Chemical Engineering Science*, 57, pp. 2825-2835, 2002.

Li, X. and H. Kunieda, "Catanionic Surfactants: Microemulsion Formation and Solubilization", *Current Opinion in Colloid and Interface Science*, Vol. 8, pp. 327-336, 2003.

Liu, Q., M. Dong, W. Zhou, M. Ayub, Y.P. Zhang and S. Huang, "Improved Oil Recovery by Adsorption-desorption in Chemical Flooding", *Journal of Petroleum Science and Engineering*, 2004. (in press)

Martinelli, F.N. and B.W.J. Lynch, "Factors Affecting the Efficiency of Dispersants", LR 363 (OP), Warren Spring Laboratory, Stevenage, 18 p., 1980.

Mackay, D., "Effectiveness of Chemical Dispersants Under Breaking Wave Conditions", in *The Use of Chemicals in Oil Spill Response*, STP 1252, American Society for Testing and Materials, Philadelphia, PA, pp. 310-340, 1995.

McAuliffe, C.D., "The Use of Chemical Dispersants to Control Oil Spills in Shallow Nearshore Waters", STP 1018, American Society for Testing and Materials, Philadelphia, PA, pp. 49-72, 1989.

Moet, A., M.Y. Bakr, M. Abdelmonim and O. Abdelwahab, "Factors Affecting Measurements of the Efficiency of Spilled Oil Dispersion", *Preprints - Symposium on General Papers and Poster*

Session for the Division of Petroleum Chemistry, 210 National Meeting, American Chemical Society, Vol. 40, pp. 564-566, 1995.

Moles, A., L. Holland and J. Short, "The Effectiveness of Corexit 9527 and 9500 in Dispersing Fresh, Weathered and Emulsion of Alaska North Slope Crude Oil Under Subarctic Conditions", Prince William Sound Regional Citizens' Advisory Council, Anchorage, AK, 24 p., 2001.

Moles, A., L. Holland and J. Short, "Effectiveness in the Laboratory of Corexit 9527 and 9500 in Dispersing Fresh, Weathered and Emulsion of Alaska North Slope Crude Oil Under Subarctic Conditions", *Spill Science and Technology Bulletin*, 7, pp. 241-247, 2002.

Mollet, C., Y. Touhami and V. Hornof, "A Comparative Study of the Effect of Ready-Made and In Situ Formed Surfactants on Inter-facial Tension Measured by Drop Volume Tensiometry", *Journal of Colloid and Interface Science*, 178, pp. 523-530, 1996.

Moosai, R. and R.A. Dawe, "Gas Attachment of Oil Droplets for Gas Flotation for Oily Wastewater Cleanup", *Separation and Purification Technology*, 33, pp. 303-314, 2003.

Park, S-K. and A.R. Bielefeldt, "Equilibrium Partitioning of a Non-ionic Surfactant and Pentachlorophenol between Water and a Non-aqueous Phase Liquid", *Water Research*, 37, pp. 3412-3420, 2003.

Peabody, C.H., "Freshwater Dispersant Study", in *Proceedings of the Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, ON, pp. 265-274, 1982.

Prosser, A.J. and E.I. Franses, "New Thermodynamic/Electrostatic Models of Adsorption and Tension Equilibria of Aqueous Ionic Surfactant Mixtures: Application to Sodium Dodecyl Sulfate/sodium Dodecyl Sulfonate Systems", *Journal of Colloid and Interface Science*, 263, pp. 606-615, 2003.

Sabatini, D.A., E. Acosta and J.H. Harwell, "Linker Molecules in Surfactant Mixtures", *Current Opinion in Colloid and Interface Science*, 8, pp. 316-326, 2003.

Sayyouh, M.H., M.S. Al-Blehed and A.M. Attla, "The Effect of Alkaline and Polymer Additives on Phase Behaviour of Surfactant-oil-brine System at High Salinity Conditions", *Revue de L'Institut Francais du Petrole*, 48, pp. 359-369, 1993.

Scott, B.F., E. Nagy, J.P. Sherry, B.J. Dutka, V. Glooschenko, N.B. Snow and P.J. Wade, "Ecological Effects of Oil-Dispersant Mixtures in Fresh Water", in *Proceedings of the 1979 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp. 565-571, 1979.

Song, F.Y. and M.R. Islam, "Effect of Salinity and Rock Type on Sorption Behaviour of Surfactants as Applied in Cleaning of Petroleum Contaminants", *Journal of Petroleum Science and Engineering*, 10, pp. 321-336, 1994.

Sterling, M.S., J.S. Bonner, A.N.S. Ernest, C.A. Page and R.L. Autenreith, "Chemical Dispersant

Effectiveness Testing: Influence of Droplet Coalescence", *Marine Pollution Bulletin*, 48, pp. 969-977, 2004.

Vaughn, S.L., C.N.K. Mooers and S.M. Gay, "Physical Variability in Prince William Sound during the SEA Study (1994-98)", *Fisheries Oceanography*, 10(Suppl. 1), pp. 58-80, 2001.

Watt, S.L., D. Tunaley and S. Biggs, "The Formation of Water-in-oil Microemulsions Using a Concentrated Saline Aqueous Solution", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 137, pp. 25-33, 1998.

Wells, P.G. and G.W. Harris, "Dispersing Effectiveness of Some Oil Spill Dispersants: Testing with the 'Mackay Apparatus'", *Spill Technology Newsletter*, 4, pp. 232-241, 1979.

Wolfe, M.F., G.J.B. Schwartz, S. Singaram, E.E. Mielbrecht, R.S. Tjeerdema and M.L. Sowby, "Effects of Salinity and Temperature on the Bioavailability of Dispersed Petroleum Hydrocarbons to the Golden-Brown Algae, *Isochrysis galbana*", *Archives of Environmental Contamination and Toxicology*, 35, pp. 268-273, 1998.

Wolfe, M.F., H.E. Olsen, K.A. Gasuad, R.S. Tjeerdema and M.L. Sowby, "Induction of Heat Shock Protein (hsp)60 in *Isochrysis galbana* Exposed to Sublethal Preparations of Dispersant and Prudhoe Bay Crude Oil", *Marine Environmental Research*, 47, pp. 473-489, 1999.

Wu, J., Y. Xu, T. Dabros and H. Hamza, "Development of a Method for Measurement of Relative Solubility of Nonionic Surfactants", *Colloids and Surfaces A: Physiocochem Engineering Aspects*, 232, pp. 229-237, 2004.

Ysambertt, F., R. Anton and J-L. Salager, "Retrograde Transition in the Phase Behaviour of Surfactant-Oil-Water Systems Produced by an Oil Equivalent Alkane Carbon Number Scan", *Colloids and Surfaces A; Physicochemical and Engineering Aspects*, 125, pp. 131-136, 1997.

Yu, H., B.K. Man, L.L.Chan, M.H. Lam, P.K. Lam, L. Wang, H. Jin and R.S. Wu, "Cloud-point Extraction of Nodularin-R from Natural Waters", *Analytica Chimica Acta*, 509, pp. 63-70, 2004.

Zhang, L., L. Luo, S. Zhao, Z-C. Xu, J-Y An and J-Y Yu, "Effect of Different Acidic Fractions in Crude Oil on Dynamic Interfacial Tensions in Surfactant/alkali/model Oil Systems", *Journal of Petroleum Science and Engineering*, 41, pp. 189-198, 2004.

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Colon, Betzy
Sent: Wed 4/15/2015 1:01:27 AM
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Thanks so much Robyn! Will be in touch.

Betzy

From: Conmy, Robyn [mailto:Conmy.Robyn@epa.gov]
Sent: Tuesday, April 14, 2015 3:03 PM
To: Colon, Betzy
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Here are the cv and the signed COI form

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Colon, Betzy [mailto:BColon@versar.com]
Sent: Tuesday, April 14, 2015 9:07 AM

To: Conmy, Robyn
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Robyn,

Would it be possible for you to send me an electronic copy of your CV today? It can be a draft version if that helps. I'm getting ready to send BSEE our initial list of reviewers, but also need to include a brief summary of their background/qualifications.

Thanks so much,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

VERSAR

Direct Line: (703) 642-6727

Mobile: (352) 514-5471

Fax: (703) 642-6809

Email: bcolon@versar.com

Visit us at: www.versar.com

From: Colon, Betzy
Sent: Thursday, April 9, 2015 12:00 PM
To: 'Conmy, Robyn'
Cc: Schubauer-Berigan, Joseph; Gilliland, Alice
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Robyn,

I am glad to hear that you are interested and available to participate as a reviewer. I will send you some additional information in a separate email.

Alice, thank you again for forwarding my email along.

Best regards,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

VERSAR

Direct Line: (703) 642-6727

Mobile: (352) 514-5471

Fax: (703) 642-6809

Email: bcolon@versar.com

Visit us at: www.versar.com

From: Conmy, Robyn [mailto:Conmy.Robyn@epa.gov]
Sent: Thursday, April 9, 2015 9:54 AM
To: Colon, Betzy
Cc: Schubauer-Berigan, Joseph; Gilliland, Alice
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hello Ms. Colon,

I am happy to serve as a reviewer for the BSEE report.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Gilliland, Alice
Sent: Thursday, April 09, 2015 8:17 AM
To: Conmy, Robyn
Cc: Schubauer-Berigan, Joseph
Subject: FW: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Robyn,

Can you please reach out to Betzy Colon next week (after you return) if you have time to be a peer reviewer on this?

Thanks,

Alice

From: Colon, Betzy [mailto:BColon@versar.com]
Sent: Wednesday, April 08, 2015 3:32 PM
To: Gilliland, Alice
Subject: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Alice,

I tried leaving a message on your phone but not sure if I was successful. I may have hung up before the message was saved. The reason I contacted you is because we are conducting a peer review for the Bureau of Safety and Environmental Enforcement (BSEE) on dispersants and wanted to see if someone from your team might be interested in participating as a reviewer. I know Dr. Venosa used to conduct research in this area but not sure if someone from EPA has taken over this research after he retired.

I provided specific information below on the peer review. Feel free to forward to anyone on your team who may be able to participate in this peer review.

Thank you,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

VERSAR

Direct Line: (703) 642-6727

Mobile: (352) 514-5471

Fax: (703) 642-6809

Email: bcolon@versar.com

>>

My name is Betzy Colon and I work for an environmental consulting firm that is supporting the Department of the Interior (DOI) Bureau of Safety and Environmental Enforcement (BSEE) in conducting an external peer review of the draft document titled "Comparative Testing of Corexit EC9500A, Finasol OSR 52, Accell Clean DWD, and ZI 400 at Ohmsett in a Simulated Arctic Environment." The peer review will be a letter peer review with no teleconference or in-person meeting required. I am writing to see if you would be interested in participating in the peer review scheduled to begin in early May.

BACKGROUND:

BSEE has requested an external peer review of the draft report entitled "Comparative Testing of Corexit EC9500A, Finasol OSR 52, Accell Clean DWD, and ZI 400 at Ohmsett in a Simulated Arctic Environment," which was prepared by BSEE. Part of BSEE's research is committed to ensuring that functional, safe, and environmentally responsible oil spill response methods are identified and used under appropriate conditions. Understanding oil spill response technologies for use in the Arctic is crucial for the U.S. government and industry to develop robust spill response plans. In February of 2014, BSEE conducted independent dispersant effectiveness testing to compare available formulations. Several products were tested under mesoscale simulated arctic conditions at the Ohmsett facility. The study was conducted in order to better understand and compare the effectiveness of various dispersants under simulated Arctic test conditions. Four dispersants were selected from the EPA's NCP Product Schedule and tested on an Alaskan crude oil: Corexit® EC9500A, Finasol® OSR 52, Accell® Clean DWD, and ZI 400.

The objective of this letter-style peer review is for BSEE to receive written comments from individual experts on the scientific merit of the report, appropriateness of the methods used, quality of the data, and the overall strengths and limitations of the study.

LENGTH OF PAPERS:

The draft document to be reviewed contains approximately 25 pages of main text, including tables and figures, and 55 pages of references and appendices.

DUTIES OF REVIEWER:

Your primary function as a peer reviewer would be to evaluate and provide written comments on the document and answer seven charge questions.

We are identifying approximately six to seven scientific experts from which five will be selected to serve as peer reviewers. The reviewers will be senior scientists with expertise/experience in oil spill response in Arctic waters and a demonstrated understanding of the methods utilized to understand the efficacy/effectiveness of chemical dispersant use.

TIMELINE:

We are expecting to select reviewers within the next few weeks in preparation to begin the review in early May. Reviewers will have approximately six weeks to complete their reviews and prepare written comments, following receipt of the materials and charge questions.

COMPENSATION:

An honorarium is being provided for the peer review and will be discussed if you are interested and available to participate in the review.

NEXT STEPS:

If you are interested in participating, please provide the following information:

1. An electronic copy of your CV.

2. Complete contact information (address, phone number, email).

3. Whether you will be entering this agreement as a consultant or a subcontractor through your company (subcontract - only applicable for those people that work for companies).

Once I've received the information requested above, I will send you our conflict of interest questions for you to answer and return via e-mail, along with forms requiring your signature. Before participating, you will need to confirm that there are no conflict of interest issues, either real or perceived.

We are hoping to make selections within the next few weeks and, as a result, would appreciate a prompt response from you.

Thanks, and I look forward to hearing from you.

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

VERSAR

Direct Line: (703) 642-6727

Mobile: (352) 514-5471

Fax: (703) 642-6809

Email: bcolon@versar.com

Visit us at: www.versar.com

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Bryan, Elisha[Bryan.Elisha@epa.gov]
From: Holder, Edith
Sent: Thur 6/11/2015 4:43:30 PM
Subject: FW: SEA BRAT #4 Sample Inquiry

Robyn,

Is this OK for Elisha to respond to the manufacturer or do you or someone in OEM want to take this as the protocol is in the final stages of approval?

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Bryan, Elisha
Sent: Thursday, June 11, 2015 11:51 AM
To: Holder, Edith
Subject: Fw: SEA BRAT #4 Sample Inquiry

Edie,

Its been so long, I had to think what MDL of DCM was, lol.

I found a good contact for Sea Brat Dispersant, but he wants data sent to him. I assume it is the same as SWA, can not send anything, but will be published for everyone to see and none of the Dispersants will be directly named in the publication?

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: John Sheffield <alabastercorp@gmail.com>
Sent: Thursday, June 11, 2015 11:31 AM
To: Bryan, Elisha
Subject: Re: SEA BRAT #4 Sample Inquiry

Hello,

I can provide a sample if you pay shipping.

But I want written/ email of all the test results, publications, etc.

Where are the result going to be published, etc.

John Sheffield

On Thu, Jun 11, 2015 at 10:19 AM, Bryan, Elisha <Bryan.Elisha@epa.gov> wrote:

Good Afternoon,

The U.S. Environmental Protection Agency will be conducting a series of Dispersant Efficacy experiments using the newly proposed Baffled Flask Test for inclusion in the 40 CFR Appendix C to Part 300 Subpart J.   I am a contractor with EPA's Office of Research and Development, National Risk Management Research Laboratory (NRMRL), Land Remediation and Pollution Control Division (LRPCD), working on this research.

As your product is listed on the U.S. EPA National Contingency Plan Product Schedule, we would like to include your product in our research and are interested in procuring a small quantity.   I am contacting all manufacturers listed so that we can take into consideration the different characteristics of the dispersants.

This research will not change the current status of your product on the Product Schedule. More information on the proposed revisions and who to contact for comments can be found here: https://www.federalregister.gov/articles/2015/01/22/2015-00544/national-oil-and-hazardous-substances-pollution-contingency-plan#h-44.

Could you please send me a price quote for one liter / quart of *SEA BRAT #4*?

Thank you,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Ryan, Scott A[Scott.Ryan@dfo-mpo.gc.ca]
From: Robinson, Brian
Sent: Fri 8/21/2015 8:02:17 PM
Subject: First data tables & figures
Stacked Fluorometry Plots Summary - BTEX Calibrated.docx
Stacked Fluorometry Plots Summary - TPH Calibrated.docx
Stacked Fluorometry Plots Summary.docx
Table 1-8 Daily Log Sheets.docx

Hi Robyn,

I thought I would start sending you data as we get things finished, rather than waiting until everything is done at the end. Attached you will find the following:

-       Tables with all of the wave tank daily log data

-       Figures will all the stacked fluorometry plots – three separate documents for factory calibrated values, TPH and BTEX

The next data dump should include the LISST summary figures and the chemistry data. If you would prefer me to upload files rather than send them over email, please let me know.

Have a nice weekend!

Brian

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Holder, Edith
Sent: Thur 5/14/2015 8:30:53 PM
Subject: Dispersants in the lab

Current Inventory of Oil Spill Dispersants Line Items # 10-15 (May 2015)

Accell Clean DWD	Finasol OSR52	Saf-Ron Gold
Corexit 9500	JD-2000	SX-100
Dispersit SPC1000	Nokomis 3-AA	ZI-400
FFT Solution	Nokomis 3-F4	

These are the dispersants that we have in the laboratory. SW-100 is no longer listed on the NCP list, but…we have it.

So we have the 6 listed in "The Table." Saf-Ron Gold, JD2000, and Dispersit are older stock from before. Nokomis 3AA and ZI-400 are brand new. Only Corexit is from the same lot used for creating "The Table."

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

To: Campo-Moreno, Pablo (campomp)[campomp@UCMAIL.UC.EDU]
Cc: Zhang, Yu (zhang4y5)[zhang4y5@mail.uc.edu]; Holder, Edith[holder.edith@epa.gov]; Zhuang,
Mobing (zhuangmg)[zhuangmg@mail.uc.edu]; Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Deshpande, Ruta (deshpars)
Sent: Mon 6/8/2015 7:18:12 PM
Subject: Re: Result of Finasol Experiment
WA405Task1.2-results-GCMS.docx
WA405Task1.2-results-Iatroscan.docx

Please find the attached files. Thank you.

Ruta Suresh Deshpande
Graduate Assistant

Department of Biomedical, Chemical
and Environmental Engineering
University of Cincinnati
Cincinnati, OH 45221-0012
deshpars@mail.uc.edu
Tel:513-641-8677

From: Campo-Moreno, Pablo (campomp) <campomp@UCMAIL.UC.EDU>
Sent: Monday, June 8, 2015 7:10 PM
To: Deshpande, Ruta (deshpars)
Cc: Zhang, Yu (zhang4y5); Holder, Edith; Zhuang, Mobing (zhuangmg); Robyn Conmy
Subject: Re: Result of Finasol Experiment

Ruta,

Could you please send over your data along with your SARA chromatograms?
Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor
University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
766 ERC
Cincinnati, OH 45221-0012
PH:(513)-556-3637
Fax: (513)-556-4162
campomp@ucmail.uc.edu

It is a capital mistake to theorize before one has data. Insensibly one begins to
twist facts to suit theories, instead of theories to suit facts.
The adventures for Sherlock Holmes

On Jun 8, 2015, at 3:07 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Thank you for sending and for the update!

Pablo, can you send to Edie and I the figures from the dilbit and ANS degradation results? We didn't walk away with our hard copies. Also, Ruta's SARA plots would be helpful too.

Thanks,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Zhang, Yu (zhang4y5) [mailto:zhang4y5@mail.uc.edu]
Sent: Monday, June 08, 2015 1:34 PM
To: Conmy, Robyn; Holder, Edith

Hi! Robyn and Edith.

Please find the Finasol result in the attachment. Let me know if there is any problem with it. Thanks!

Regards,

Yu